

Wood Extractives: Main Families, Functional Properties, Fields of Application and Interest of Wood Waste

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Abstract

The extractives contained in wood are compounds with a very high added value in various fields (e.g., pharmaceuticals, cosmetics, agri-food). These extractives can be classified into four groups: lipid components (terpenes and terpenoids), waxes and fats, phenolic compounds, and alkaloids. This review is particularly focused on the description of the main families of extractives contained in wood waste, with their properties and the potential applications made to date. It also makes a brief report on some conventional techniques for extracting wood extractives, with an eye toward recovering wood waste in our country. These extractives, particularly phenolic compounds, fall into several categories: simple phenols, lignans, flavonoids and tannins. They have chemical and biological properties such as antioxidants, antiradicals, anti-termites, antifungals, anticancer, inhibitors of type 1 human immunodeficiency virus, antimutagenics, and antimicrobial properties. They are also used in food preservation as well as wood protection. This review sums up the interest that should be focused on the availability in large quantities of wood waste in our environment, which, far from being a problem, could be the solution to certain current and future problems.

Wood, an important source of raw materials, is an essential material in the world because of its various possible uses in industry, construction, agriculture, and other fields. Indeed, wood is an important source of income in some countries such as Côte d'Ivoire. However, given the growing demand for wood due to its importance, we have an increase in logging and a large amount of wood waste produced by processing companies in our country. It is estimated that only 30 percent of each felled tree is recycled, whereas 70 percent of the tree ends as the waste produced (Saha 2015). Most wood waste and byproducts are subject to material recovery (e.g., paper pulp, particle board, insulation) or energy recovery as biofuels to produce heat or electricity (Meullemiestre 2014). Yet in the tree, apart from the main constituents of the cell wall (cellulose, hemicellulose, and lignin) that form the largest part of the wood (Roesyadi 1987, Alén et al. 1995), several families of chemical compounds (primary and secondary metabolites) are also present (Niamké et al. 2011). Low molecular weight compounds (as opposed to wood macromolecules) are better known as extractives because they can be easily extracted

by the choice of suitable solvents (e.g., organic, aqueous; Stevanovic and Perrin 2009, Meullemiestre 2014, Bruneton 2016) and are found in the porous structure of the wood. Extractives include a whole range of compounds, most of which are secondary metabolites (i.e., compounds that are not essential for plant growth). There is minimal difference in the chemical structure of different species of trees (or shrubs) at the level of the three main constituents of wood—

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cellulose, lignin, and hemicelluloses—as opposed to the great variation in composition of extractives from one species to another (Hon and Shiraishi 2001). Indeed, the content of extractives, which can range from 5 to 20 percent, as well as their nature vary according to the species, geographical site, genetics, or season. The study by Hon and Shiraishi (2000) confirms that tropical woods have more extractive content than do woods from temperate regions. Also, literature (Nzokou et al. 2005, Mburu et al. 2007, Mounguengui et al. 2016, Saha et al. 2018) indicates that many tropical woods contain high levels of extractives. This particularly reinforces the interest shown in them with a view to their valuation. Indeed, extractives present in wood are responsible for its color (Amusan 2003, Gierlinger et al. 2004), its smell, its hygroscopy (Krutul 1992), its natural durability (Barbosa et al. 2007, Niamké et al. 2011), its physical and mechanical properties such as dimensional stability (Royer et al. 2010), and its acoustic properties (Minato and Sakai 1997). Many extractives exhibit particular biological activities; wood extracts have been used for centuries as sources of traditional remedies (Arnason et al. 1981). Known for their properties and derived from renewable resources, extractives are already the subject of much research and development in various fields (pharmaceutical, agri-food, cosmetics; Mounguengui 2008, Huang et al. 2009). Wood extractives are little or not at all exploited in Côte d'Ivoire. However, they inhibit the growth of wood alteration agents (bacteria, termites, and fungi; Niamké et al. 2012, Maranhão et al. 2013) and have biocidal properties (Haluk and Jodin 1994, Haluk and Roussel 2000). Extractives confer sustainability by infusing the wood of less durable species with extracts from the wood of more resistant species; they constitute active substances that can be used in the formulation of wood preservation products (Brocco et al. 2017, Rodrigues et al. 2012). The possible uses of wood extractives and the availability of large quantities of wood waste in our environment, mainly in Côte d'Ivoire, offer prospects for better recovery of this wood waste. Our work therefore presents advances related to the fields of application of wood extractives (mainly tropical woods) as well as the potential recovery of their waste (abundant in the industrial environment) in the agricultural area. After a brief presentation of extractives and the main families of extractives, we review fields of application of wood extractives, particularly in agriculture, with regard to their functional properties.

Wood Extractives

Wood, like wood waste, is mainly made up of three natural polymers (cellulose, hemicellulose, and lignin), which comprise the cell wall and form most of the wood (Roesyadi 1987, Alén et al. 1995). Several families of secondary metabolites are also present in the tree, in the wood itself, but also in the leaves, roots, bark, and nodes. Extractives organic substances represent about 2 to 5 percent of the composition of softwoods, 3 to 8 percent of temperate hardwoods, and up to 18 to 22 percent of tropical woods (Mosedale et al. 1998). These molecules specific to each forest species, despite their low concentration in the wood compared with that of the three structural polymers, are responsible for the variability of several properties within the various species but also within the same tree (Schultz et al. 1995, Mosedale et al. 1998, Schultz and

Nicholos 2000, Lacandula 2002, Amusan et al. 2007). These metabolites, essential to the adaptation and survival of the tree, fulfill the role of defense by constituting a chemical or physical barrier against wood degradation agents. The presence of extractives in the heartwood strongly influences the natural durability, olfactory, physico-mechanical, or even acoustic properties of the wood (Stevanovic and Perrin 2009). Hawley et al. (1924) first highlighted the link between natural sustainability and extractives; then many researchers, such as Taylor et al. (2006) and Santana et al. (2010), have shown that the natural durability of a wood is linked to the nature of the extractives compounds it contains. Extractives, synthesized during duraminization, contribute to the robust biological resistance of wood against xylophagous organisms without the need to resort to preservation treatments or protection methods. The *in vitro* studies performed by Oliveira et al. (2010) and Kirker et al. (2013) showed that, once extracted, the wooden blocks were more easily degraded by lignivorous organisms (fungi and termites). Extractives contribute a lot to the protection of wood against lignivorous organisms. Different families, genera, and species of wood contain different types of extractives. Some of these molecules are true 'chemotaxa'; i.e., they are markers whose presence is characteristic of the family, genus, or species. These chemotaxons make it possible to identify the plant material ('chemical signature'). For example, the *Cupressaceae* family is the only source of terpene compounds of an aromatic nature, the tropolones, including the thuyaplicins found in cedar heartwood (Stevanovic and Perrin 2009). The diversity of structures of these molecules allows them to be classified into several families (Stevanovic and Perrin 2009): terpenoids (including tropolones), waxes and fats, polyphenols (benzene compounds containing several phenolic hydroxyls), salts of organic acids, complex carbohydrates, and nitrogen compounds (proteins, alkaloids). Extracts from different woods and barks are always complex mixtures and their composition depends on the extraction method used (Royer 2008, Diouf et al. 2009).

Extraction methods

Extractives are particularly localized in the lumen (Gandini and Belgacem 2002) and cell wall or in specialized cells such as the resin canals in conifers, as well as in the interstitial spaces, and can be easily extracted by the choice of suitable solvents (e.g., organic, aqueous; Stevanovic and Perrin 2009, Meullemiestre 2014, Bruneton 2016). We present a brief description of the classical methods of extraction (solid or liquid) for the sake of understanding.

Soxhlet extraction.—This extraction technique was named after Baron Von Soxhlet, who created this procedure in the mid-19th century (Mittra 2003). This method is based on reflux and siphoning to constantly extract the sample from the plant with fresh solvent, thus combining the processes of percolation and reflux using heat (Patra et al. 2018). The Soxhlet is one of the most used techniques for extraction. Some of the advantages of Soxhlet extraction are the preservation of the sample in contact with the fresh solvent, maintenance of a relatively high extraction temperature resulting from the heat of the distillation flask, absence of the need for filtration after leaching, simplicity of operation, and low cost. The main disadvantages of Soxhlet extraction are the long extraction time, use of a large amount of solvent, the impossibility of using agitation to

speed up the process, and the possibility of thermal decomposition of sensitive compounds when exposed to heat (Wang and Weller 2006).

Infusion.—This is an extraction technique widely used in traditional medicine (Patra et al. 2018). The infusion is prepared by adding a small amount of plant material to the solvent at high temperature, which allows extraction in a short time (Gamboa-Gómez et al. 2017). To facilitate the extraction of compounds, plant material should be cut into small pieces (Rakotoniana et al. 2018). This method produces extracts abundant in essential oil (Malca-Garcia et al. 2019). However, it has the disadvantage of using a large amount of solvent (Tiwari 2015). Also, the use of a high temperature can cause the degradation of thermolabile compounds (Malca-Garcia et al. 2019).

Maceration.—This technique is considered a simple extraction process. It consists of immersing the wood sample for a long period in a solvent to extract the soluble components (Patra et al. 2018). The greatest advantage of this method is its simplicity and the fact that it does not risk degrading thermolabile compounds, but it does not allow the bioactive compounds to be completely extracted from the plant.

Steam distillation and hydrodistillation.—In those processes that are suitable for distillation of heat-sensitive compounds, the applied heat is the primary cause of disruption of the cellular structure of the plant material, allowing the heat-sensitive compounds to be released. The heating temperature plays an important role because it must be sufficient to release the desired compounds (Tongnuanchan and Benjakul 2014). In steam distillation, water is boiled in one compartment and the resulting vapor passes through plant matter in another compartment. Alternatively, direct steam can be introduced into the sample for extraction. In hydrodistillation, however, water and plant material are placed in the same vessel and boiled together (Selvamuthukumaran and Shi 2017). Besides the similarity of these two extraction methods, steam distillation allows a higher yield of essential oils and a better collection of volatile compounds. The small number of volatile compounds recovered during hydrodistillation is due to the hydrolysis reaction caused by the combined action of water and high temperature, which can lead to degradation of certain compounds. On the other hand, distillation at steam can avoid this degradation and allow production of higher quality essential oils because the plant material is not in direct contact with water (Ali et al. 2019).

Large families of extractives

Wood, like its waste that we find abandoned in the environment, is made up of extractives compounds including waxes, fats, terpenes and terpenoids, fatty acids, monosaccharides, alkaloids, and phenolic compounds. Extractives can be extracted from waste and then used for other purposes, and for this they can be classified into four categories. The first category includes terpenes and terpenoids, and some of these extracts are also called gems. The second category includes aliphatic compounds such as saturated and unsaturated fatty acids, alkanes, and fatty alcohols (e.g., triglyceride, palmitic acid, stearic acid). A third category concerns phenolic compounds. This large class includes simple phenols (vanilin), lignans (pinosresinol, hinokiresinol), flavonoids, tannins, and stilbenes (Hillis

1975, Fengel and Wegner 1989, Jodin 1994, Saha 2015). The fourth category comprises the alkaloids.

Terpenes and terpenoids

Terpenes.—Terpenes are synthesized by the epithelial cells (specialized tissue of the parenchyma), which line the resin canals. Terpenes have a basic formula of multiples of isoprene units (C_5H_8)_n (Fig. 1). They can be classified according to the number of isoprene units:

- $n = 2$: monoterpenes. These are the most common. They have the formula $C_{10}H_{16}$ and include many isomers (e.g., pinenes, germacrene, cadinene).
- $n = 3$: sesquiterpenes, $C_{15}H_{24}$ (β -Cadinene).
- $n = 4$: diterpenes, $C_{20}H_{32}$ (e.g., pimaradiene, larixol, manoyloxide).
- $n = 5$: sesterpenes ($C_{25}H_{40}$).
- $n = 6$: triterpenes ($C_{30}H_{48}$) (e.g., betulinic acid, oleanols).
- $n = 8$: polyterpenes ($C_{40}H_{64}$) (gutta-percha).

Terpene compounds have several roles in the tree, such as resistance to diseases and attacks by microorganisms, and creation of odor (nerolidol, farnesol, cedrol). Terpenes protect plants and wood against pathogens such as molds, fungi, and bacteria and can attract pollinating insects or repel herbivores. Thus, following an attack by a parasite or predators, the concentrations of these compounds increase. Tropolones are compounds responsible for the natural durability of certain woods. Saniewska and Jarecka (2008) have shown that hinokitiols (β -thujaplicin) are able to strongly inhibit the growth of fungi such as *Coriulus versicolor*, *Phanerochaete chrysosporium*, *Poria placenta*, and *Gloeophyllum trabeum* (Saniewska and Jarecka 2008, Nuutinen 2018). Sterols are compounds of the cell membrane that participate in its stabilization. Phytol is a diterpene that is part of the structure of chlorophyll.

Terpenoids.—Terpenoids are molecules that contain oxygenated groups (Fig. 2). They are classified into mono, di, oligo, and polyterpenes (Bugrein and Bujassoum 2016); these are the compounds of terpene derivatives, and have forms such as alcohol (-OH), acid (-COOH), ketone (=O).

Terpenoids are anticancer compounds. Their mechanisms of action are varied and include processes such as neutralization of oxidative stress, potentiation of endogenous antioxidants, enhancement of detoxification potential, and others. Betulinic acid is a pentacyclic triterpenoid used as a folk remedy by Native Americans. It is a molecule that is adsorbed by intestinal cell membranes (Sharma et al. 2017). Monoterpenes (Camphene, (R)-camphor, (R)-carvone, 1,8-cineole, cuminaldehyde, (S)-fenchone, geraniol, (R)-linalool, (1R, 2S, 5R)-menthol, myrcene, and thymol) have antifungal activities against certain phytopathogenic fungi such as *Rhizoctonia solani* and *Fusarium oxysporum*, the latter causing green and black mold (Marei et al. 2012). For example, Garcia et al. (2008) demonstrated that L-carvone from *Pinus sylvestris* strongly inhibits fungal growth. Turley et al. (2006) demonstrated that these compounds are more powerful in destroying *Escherichia coli*. Betulins are triterpene pentacyclics present in birch (*Betula* spp.) bark, they have specific qualities (antimold and antibacterial). Lupeol is a triterpene with chemopreventative, cytotoxic, and antioxidant effects.

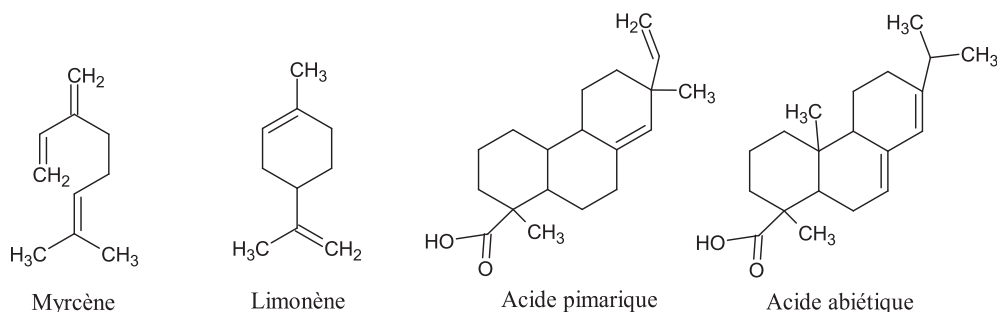


Figure 1.—The structures of some main known terpenes.

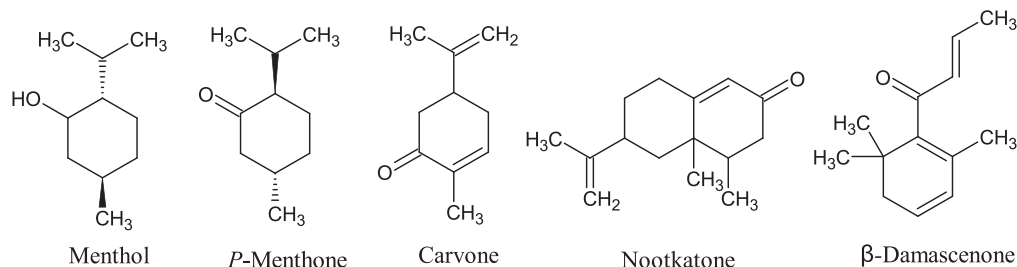


Figure 2.—The structures of some main known terpenoids.

Saturated and unsaturated fatty acids

Fatty acids, molecules that are scarce in free form in fresh fats, are hydrophobic aliphatic chain carboxylic acids, saturated or unsaturated depending on whether they contain or do not contain double bonds. They can contain 2 to 24 or more carbon atoms (Rustan and Drevon 2005). The general chemical formula of saturated fatty acids is: $\text{CH}_3-(\text{CH}_2)_n-\text{COOH}$. Unsaturated fatty acids can contain between one and six double bonds and are said to be monounsaturated or polyunsaturated, depending on the case. African ecosystems are full of many multipurpose plant species that remain wild and underexploited. In the tropics, there are many sources of vegetable oils available but not exploited or not used optimally (Dahouenon-Ahoussi et al. 2012). In the case of *Griffonia simplicifolia*, this plant belongs to the *Fabaceae* family (Kumar et al. 2010, Espitalier 2014, Mehta et al. 2015) and is native to the forests of the coasts of Central and West Africa, in particular Gabon, Liberia, Côte d'Ivoire, Ghana, and Togo (Brendler et al. 2010). It is a plant very well known to the populations thanks to its richness in curative virtues. Its seeds contain biochemical compounds, in this case fat, which can also be used in food or for other purposes. Oils are used in the preparation of various dishes or other products useful to humans (e.g., soap, cosmetics). Most often, they contain essential fatty acids for the harmonious functioning of the body (Aboubakar Dandjouma et al. 2008). Vegetable oils are sought after for their quantities and their qualities as compared with animal fats, which are saturated with saturated fatty acids. In the case of softwoods, these are esterified fatty acids derived from di- and triglycerides, or steroid esters, representing 0.15 to 0.19 percent of the dry mass in spruce (*Picea* spp.) knots (Willför et al. 2003). In softwoods, there are several fatty acids such as linoleic acid and stearic acid. There are mono, di, or triglycerides in wood extractives. Fats and waxes can

influence the pulping process and the wettability of wood (Coelho et al. 2007).

Phenolic compounds

The phenolic compounds of wood are very varied (Haslam 1998, Macheix et al. 2005). They are characterized by at least one aromatic ring with one or more linked hydroxyl groups, but above all by their biosynthetic origin. The most common biosynthetic pathway is the shikimic acid pathway. It allows the synthesis of metabolites from sugars which leads to aromatic amino acids and then, by deamination, to cinnamic acids and their many derivatives. A second pathway involves acetate, which leads to polyacetates, which often form polycyclic compounds (Stevanovic and Perrin 2009, Bruneton 2016). Derivatives carrying several hydroxyl functions are called polyphenols; they include simple phenols (Fig. 3), phenolic acids, and coumarins, as well as polymerized forms. Plant phenolic compounds have in recent years inspired gradually increasing interest on account of their supposed beneficial effects on health and the possibility of exploiting them as food ingredients (Karonen et al. 2004). They reduce the oxidative deterioration of lipids and thus enhance the capacity and nutritional value of foods (Kähkönen et al. 1999). Phenolic compounds are among the most studied compounds among secondary metabolites, but many of them have properties that are still poorly understood (Raven et al. 2000). There are >8,000 molecules identified and isolated to date, which are mainly synthesized in the plant kingdom. According to their basic skeleton, several families of natural phenolic compounds can be distinguished; e.g., simple phenols, flavonoids, quinones, stilbenes, lignans, tannins.

Functional properties.—These phenolic compounds play a preventive role against cancer and heart problems. They also have a protective effect against ultraviolet rays, pathogens, herbivores, and lipids protect against oxidation

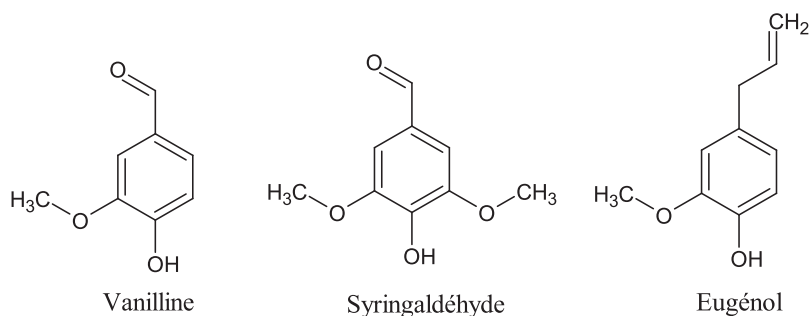


Figure 3.—Some examples of simple phenols.

of the cell membrane (Sghaier et al. 2011, Da Silva et al. 2016). Some of these polyphenolic compounds have antioxidant and antimicrobial activities, thus increasing interest in extraction of these compounds (Fernandez-Agullo et al. 2015). Other studies have shown that polyphenols have antibacterial, anticarcinogenic, and osteoinductive properties (Lišková et al. 2015). Salicylated derivatives, e.g., have anti-inflammatory, analgesic, and antipyretic properties. Among these derivatives, the best-known phenolic acid is salicylic acid (isolated from willow bark), which has been used to synthesize acetylsalicylic acid. The latter is marketed as ‘aspirin’ (Bruneton 2016).

Flavonoids.—Flavonoids are the most numerous among phenolic compounds (Raven et al. 2000). The structure of flavonoids comprises 15 carbons (C6-C3-C6), with 2 aromatic rings (C6) connected by a heterocyclic pyran ring of the 3-carbon bridge (C3; Nogales-Bueno et al. 2017); the variation as well as the hydroxylation profile of the chroman ring (C rings) are factors in the diversity of flavonoids such as anthocyanins, flavan-3-ols, flavones, flavanones, and flavonols (Fig. 4). Some flavonoids or the B ring are connected at the C3 and C4 position, such as isoflavones and neoflavonoids. Another class of flavonoid families is the Chalcones; the latter do not have the heterocyclique C ring. These structural variations are the origin of the physico-chemical properties, the biological properties attributed to these compounds (Ohmura et al. 2000, Macheix et al. 2005, Hooper and Cassidy 2006). These compounds act by different mechanisms of capture of free radicals and by chelation of metal ions.

The antioxidant capacities of many flavonoids are much stronger than those of vitamins C and E. Indeed, Flavonoids are able to scavenge free radicals directly through a hydrogen atom, the radicals are rendered inactive, where (R●) is a free radical, and (Fl-O●) represents a flavonoid phenoxy radical. The free radical (Fl-O●) formed can react

with a second radical to give a stable quinone (Pietta 2000). This antioxidant activity is known as “reactive oxygen species scavenging.” *Eucalyptus*, buckwheat (*Eriogonum* spp.), and sophora (*Sophora* spp.) are plants rich in flavonoid glycoside; they are used for the treatment of venous and capillary disorders. Pterocarpanes are flavonoids with good antifeedant activity. This is the case for naringenin, which is renowned for its antiviral, antitumor, anti-inflammatory, anti-allergic, antibacterial, anticarcinogenic, and vascular-protective activities (Arima et al. 2002). However, the antioxidant activity depends on the arrangement of the functional groups on the structure of the flavonoid. The position and total number of hydroxyl groups significantly influence the mechanism of antioxidant activity (Heim et al. 2002). The hydroxyl configuration of the B ring is the most important determinant of this activity (Burda and Oleszek 2001), whereas substitution of the A and C rings has little impact on the radical scavenging rate constants (Taubert 2003, Amic et al. 2007). These compounds serve as protection against ultraviolet radiation, pathogens, herbivores (Harborne and Williams 2000), and produce the coloring of certain flowers and fruits as well as wood. Many researchers have shown that the natural durability of certain woods is due to the presence of flavonoids. This is the case for dihydromorine and aromadendrine, which are contained in the extractives of *Acacia* essences (Schultz et al. 1995). Sirmah et al. (2009a) showed that the natural durability of *Prosopis juliflora* is due to the presence of (-) mesquitol. Flavonoids are also used in cosmetics and prevent the oxidation of cells and the release of free radicals responsible for the alteration of cells that causes their aging.

Lignans.—Lignans are dimers consisting of two phenylpropane units (C6-C3) joined by a β-β bond at the C8 carbon (Umezawa 2003). They are classified into the following eight subgroups based on how oxygen is

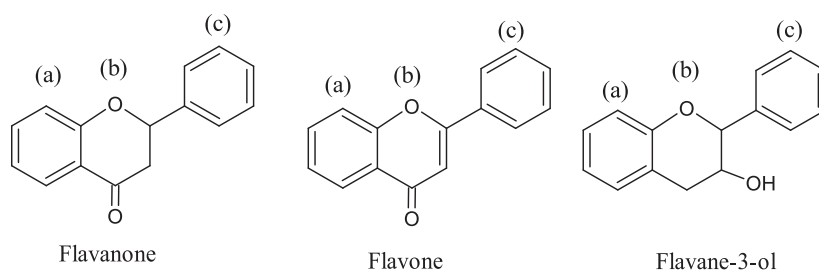


Figure 4.—Some families of flavonoids found in wood.

incorporated into the skeleton and the cyclization pattern: furofuran, furan, dibenzylbutane, dibenzylbutyrolactone, aryltetralin, aryl-naphthalene, dibenzocyclooctadiene, and dibenzylbutyrolactol (Kebbi-Benkeder 2015). Lignans appear throughout the plant kingdom (Fig. 5). These molecules can be found in abundant quantities in the knots of wood (Holmbom et al. 2003, Smeds et al. 2012, Kebbi-Benkeder et al. 2014). In some species such as spruce, lignans can represent up to 25 percent of the dry mass of the knots while normal wood contains on average only 1 percent (Willför et al. 2006). In general, the concentration of lignans is often more significant in the nodes of branches subject to mechanical stresses and loads due to environmental conditions (e.g., snow, rain, and wind; Piispanen et al. 2008). Some lignans have shown toxicity to wood-destroying agents and are very difficult to break down.

The antifungal, antibacterial, and insecticidal properties of several lignans suggest that these compounds could serve in plant defense systems; moreover, they may play a role in the regulation of plant growth (Mijnsbrugge et al. 2000). For example, syringol is a lignin pyrolysis product of hardwoods, and is the main chemical responsible for smoke flavor (Bari et al. 2009). They may exhibit antifungal activities against fungi (Pandey and Pitman 2004), as in the case of different structures identified from the bark of *obovata* essence. Apart from these properties, lignans also have antitumor (matairesinol, podophyllotoxin, and steganacine), antimutagenic (podophyllotoxin), antioxidant (nordihydroguaiaretic acid and sesaminol), and antiviral (podophyllotoxin) biological activities (Sirmah et al. 2009b). Lignans are a family of compounds that have been extensively studied for their interest in various fields, such as the pharmaceutical and agri-food fields, because of their phytoestrogenic effects (Hooper and Cassidy 2006, Lainé et al. 2007, Martins et al. 2011). In addition to these interests, lignans also have antioxidant properties (Lee et al. 2004, Zeng et al. 2014). Other lignans have antifungal properties (Kawamura et al. 2004, Céspedes et al. 2006).

Tannins.—Tannins are defined as “phenolic natural products that can precipitate proteins from their aqueous solutions” (Bruneton 2016, p. 555). Indeed, most tannins are astringent because they can complex reversibly or irreversibly with macromolecules such as proteins. They also have other biological properties including antioxidant activity and enzyme inhibition activity. Tannins are split into two groups according to their structure but also their biosynthetic origin: hydrolysable tannins and condensed tannins (proanthocyanidols; Fig. 6). Hydrolyzable tannins have often been overlooked because they are apparently

more difficult to analyze than are condensed tannins. Hydrolysable tannins are synthesized by a wide variety of trees and many of them have been used as animal feed. They can occur in wood, bark, leaves, fruits, and galls (Kumar and Vaithyanathan 1990, Naima et al. 2015). It should be noted that some species produce gallotannins or ellagitannins, while others produce complex mixtures containing gallo, ellagi, and condensed tannins. For example, *Acacia*, *Acer*, and *Fagaceae* are well known to have both condensed and hydrolysable tannins (Bate-Smith 1977, Ishimaru et al. 1987, Mueller et al. 1987).

Tannins are defined as plant-derived antinutrients because they can precipitate proteins, inhibit digestive enzymes, and reduce vitamin and mineral utilization. On the other hand, tannins have also been considered “health-promoting” components in plant-based foods and beverages. For example, tannins have been reported to possess anticarcinogenic and antimutagenic potentials, as well as antimicrobial properties. Several studies have reported on the antioxidant and antiradical activities of tannins (Amarowicz 2007). Some plants are known to be rich in tannins; this is the case of *Quercus* sp. woods, which are also widely used in the wine sector. Their woods are used to make barrels for aging wine and thus allow the creation of new aromas in wine (Zhang et al. 2015). Phlorotannin, main component of the brown algae *Ecklonia cava* used for tissue regeneration, is an inhibitor of human immunodeficiency virus type 1 (HIV-1), reverse transcriptase (RT), and protease (Ahn et al. 2004, Kim and Kim 2012). Tannin-furan foams, based on the co-reaction of condensed bark-derived tannins and thermoset furan polymers, have low thermal conductivity, are self-extinguishing, and have high fire resistance, which allowed their development for several industrial uses. One of their main drawbacks, however, is the absorption of water within the foam itself. Another problem is the rather friable surface, which is a definite drawback for some potential applications. The incorporation of fatty chains markedly decreased foam friability and increased water repellency in the bodies of these foams (Rangel et al. 2001, Sánchez et al. 2018).

Stilbenes.—Stilbenes (C6-C2-C6) are metabolites characterized by the presence of two benzene rings that are separated by an ethane or ethene bridge (Fig. 7). Of Z or E configuration, they can be free or associated with a glycoside. These compounds are mainly present in softwoods. This family of molecules has antioxidant properties (Välimäa et al. 2007), antifungals (Karppanen et al. 2007), and pharmacological and therapeutic uses (Parage 2013). They have antimicrobial and antifungal actions but would

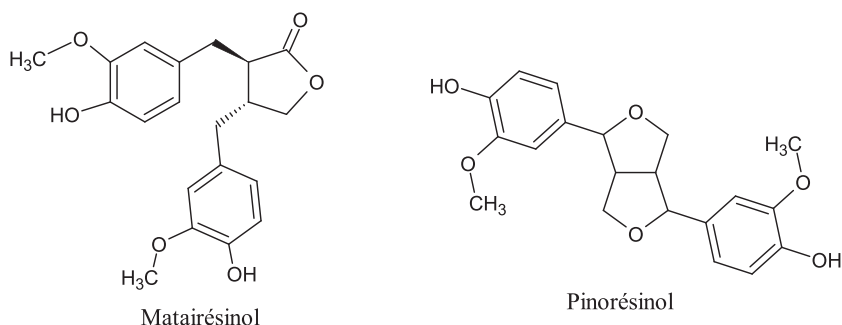


Figure 5.—Examples of lignans.

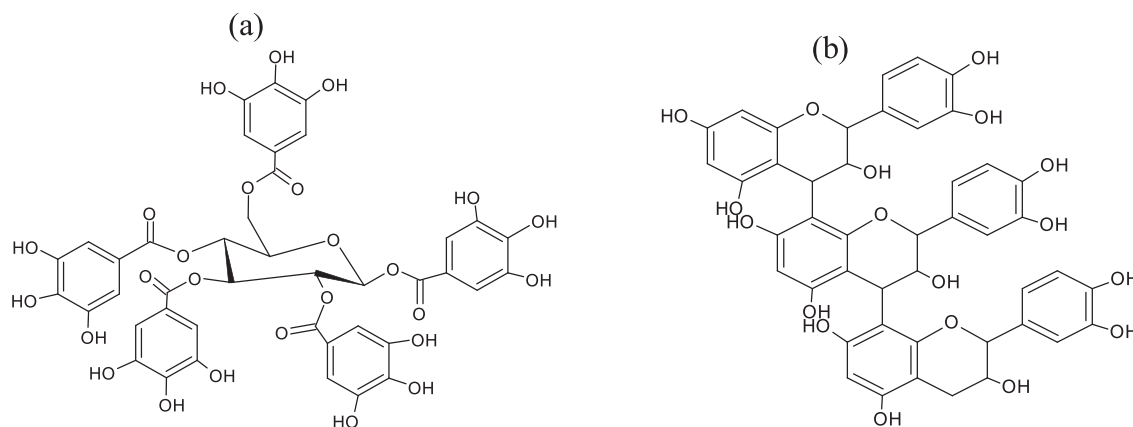


Figure 6.—Structures of hydrolysable tannin (a), condensed tannin (b).

also be antiradical and metal chelators. The best-known stilbene is resveratrol, isolated from certain fruits such as grapes. This compound is widely used in cosmetology, as well as in the production of certain food supplements, because of its antioxidant and anti-inflammatory properties (Stevanovic and Perrin 2009, Bruneton 2016). Stilbenes are synthesized by the addition of one to three molecules of malonyl-CoA to cinnamic acids, which are derived from the phenylpropane biosynthetic pathway. They have a 1,2-diphenylethene structure and consist of a C6-C2-C6 backbone. Stilbenes have two benzene rings connected by two carbons that are themselves united by a double bond. In the tree, the proportion of stilbenes varies according to the part studied, and the toxicity varies according to their structures and the bacterial or fungal strains studied (Venalainen et al. 2004, Lee et al. 2005). Pinosylvine, resveratrol, and many other stilbenes have different functions; they act as free radical scavengers, biocides, and metal chelators (Sirmah et al. 2009b).

They play a role in fungicide and protection against insects. Different species of *Combretum*, rich in stilbenes, are resistant to termites. Stilbenes are important for resistance to wood rot fungi and research has been done on inducing stilbene biosynthesis by irradiating seedlings to give better wood resistance to biodegradation (Norin 1981). They strongly influence the technological properties of wood. Stilbenes such as pinosylvine and its mono or dimethylated forms, isolated from *Picea glauca*, *Pinus resinosa*, or *Pinus banksiana*, strongly inhibit the growth of white rots such as *Phanerochaete chrysosporium* and *Trametes versicolor*, with a less significant inhibiting effect on brown rot fungi such as *Poria placenta*, *Gloeophyllum*

trabeum, and *Neolentinus lepideus* (Célimène et al. 1999, Lu et al. 2015). Stilbenes are also widely used in pharmacology (e.g., resveratrol, which has significant cardioprotective and anticancer properties; Han and Li 2004, Wang et al. 2006).

Quinones.—Quinones are oxygenated compounds resulting from the oxidation of phenols. They have a distribution restricted to certain families (e.g., *Ebenaceae*, *Fabaceae*, *Juglandaceae*). Depending on the structure of their skeleton, they are classified into several categories of quinones such as benzoquinones, naphthoquinones, or anthraquinones (Bruneton 2016). Quinones have been found in the wood of certain tropical species, notably teak (*Tectona grandis*). Teak wood contains about 0.3 percent 2-methylantraquinone (tectonic), which is a termite repellent and thus contributes to the natural durability of teak wood along with several other quinones such as naphthoquinone (Leyva et al. 1998, Thévenon et al. 2001; Fig. 8).

2-Methylantraquinone isolated from the heartwood of teak wood, and catalponol and catalponone isolated from the heartwood of *Catalpa bignonioides*, have antitermite activities (Kokutse et al. 2006, Castillo and Rossini 2010). In the natural durability of teak wood, 4',5'-dihydroxyepi-isocatalponol plays an important role against fungal attack (Niamké et al. 2012). Niamké et al. (2012) showed that this compound was a fungicide capable of inhibiting the growth of *Trametes versicolor*. In the wood of *Diospyros virginiana*, 7-methyljuglone and its isolated derivatives are also endowed with termiticidal activity (Carter et al. 1978).

Alkaloids.—The term alkaloid derives from the word alkaline and describes a molecule with the behavior of a Lewis base. According to the definition of Pelletier (1983, p. 450), alkaloids are “cyclic organic compounds containing one or more nitrogen atoms of negative oxidation state and

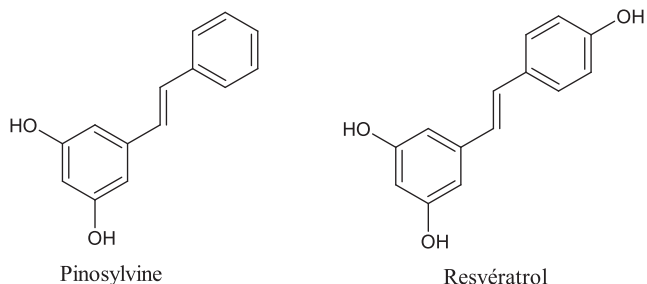


Figure 7.—Structures of some stilbenes.

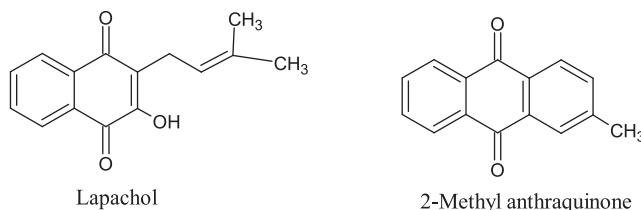


Figure 8.—Structures of quinones found in teak wood.

having a limited distribution among living beings.” The definition of the term alkaloid was recently extended by Hesse (2002) to all compounds possessing one or more nitrogen atoms, with varying degrees of basicity (Fig. 9). With >5,000 known compounds, alkaloids represent the most structurally diverse class of secondary metabolites, ranging from relatively simple molecules (such as coniine, a poison made by hemlock [*Conium maculatum*]) to incredibly complex compounds (such as batrachotoxin, a cardiotoxin and most dangerous neurotoxin in the animal world; Mann 1998). This chemical family has always attracted particular attention regarding the complexity of the structures and their potential in pharmacology. Widely used in pharmacy, some alkaloids are currently used as active ingredients in pharmaceutical specialties (Amirkia and Heinrich 2014). Many organic chemists have resorted to the organic synthesis of certain alkaloids, drawing inspiration from their chemical structures as they occur in nature. Since the 1960s, many alkaloids have been synthesized (Liu et al. 2016).

Functional properties

Alkaloids act either as a protective agent against fungi, insects, or even herbivores, as a source of nitrogen necessary for the development of the plant, as growth regulating agents similar to hormones, or as protective agents against ultraviolet radiation. Indeed, they are toxic to insects, paralyzing or killing insects that feed on them (Trematerra and Sciarretta 2002, Bouchelta et al. 2005). In medicine, alkaloids are used as major analgesics (morphine), antimalarial (quinine), to combat excess uric acid (colchicine), as a paralyzing substance (curare, caffeine), as poisons (strychnine, nicotine), as narcotics (cocaine, mescaline), as a cholinergic (pilocarpine), or as an anticancer (vinblastine, vincristine). They act directly on the nervous system with effects on consciousness and motor skills. The action on the nervous system can go as far as an antispasmodic, mydriatic, local anesthetic or analgesic, and narcotic action. *Cinchona* species contain quinoline alkaloids and indole alkaloids such as cinchonamine (Bruneton 2009).

All these alkaloids are said to have pronounced effects against *Plasmodium falciparum*. Similarly, the bark of *Alstonia boonei*, the leaves of *Chromolaena odorata* and *Carica papaya* also contain indole alkaloids; hence, there is interest in use of them in the fight against malaria.

N’Guessan et al. (2009) already reported the importance of indole alkaloids from *Chromolaena odorata* in this fight. Indole alkaloids have less effect than quinoline alkaloids in the fight against malaria but do not have side effects (such as ringing in the ears; Souleymane 2005). *Nicotiana tabacum* and *Capsicum annuum* are regularly prescribed against intestinal worms and contain tropane alkaloids and capsaicin, respectively. These alkaloids, when used to remedy stomach aches, are reputed to reduce gastrointestinal spasms and produce laxative effects. They increase intestinal peristalsis (Nacoulma-Ouédraogo 1996, N’Guessan et al. 2009). In addition, *Capsicum frutescens* prescribed for lower back pain contains capsaicin, which N’Guessan et al. (2009) described as having antirheumatic properties. Pyrrolizidine alkaloids from *Hibiscus esculentus* and indole alkaloids (agroclavine) from *Rauvolfia vomitoria* exert an oxytocic effect and are therefore useful in facilitating childbirth (N’Guessan et al. 2009). In addition, *Rauvolfia vomitoria* prescribed for the treatment of foot edema contains punarnavine (Kerharo and Adam 1974), which causes a marked and persistent increase in blood pressure with strong diuresis via action on the renal epithelium. In addition, reserpine from *Rauvolfia vomitoria* has sedative properties. This drug is used to treat states of anxiety and mentally disturbed patients, hence its empirical use in the treatment of epileptic seizures (N’Guessan et al. 2009). The effect against migraine of *Ageratum conyzoides* would be due to alkaloids, probably of the ergotamine type (Yinyang et al. 2014). Caffeine present in *Cola acuminata*, *Coffea robusta*, *Coffea arabica*, *Camellia sinensis*, and *Theobroma cacao* has competitive antagonistic effects of adenosine receptors. It is a neuromodulator limiting the release of the main excitatory neurotransmitters. This is how it causes acceleration of the heart rate with the possibility of palpitations, stimulation of the central nervous system with increased vigilance and sometimes anxiety, bronchodilation, or more precisely antagonistic effect of bronchoconstriction in asthmatics where adenosine seems to play a major role (Debry 1993). The properties of *Phyllanthus amarus*, *Myristica fragrans*, and *Annona muricata* against heartburn would be due to the presence of alkaloids, which would reduce pain and acidity of the stomach in patients suffering from gastric ulcers. Yohimbine, an indoloterpene alkaloid from the bark of *Pausinystalia johimbe* is one of the only natural aphrodisiacs known to man and the most powerful. It

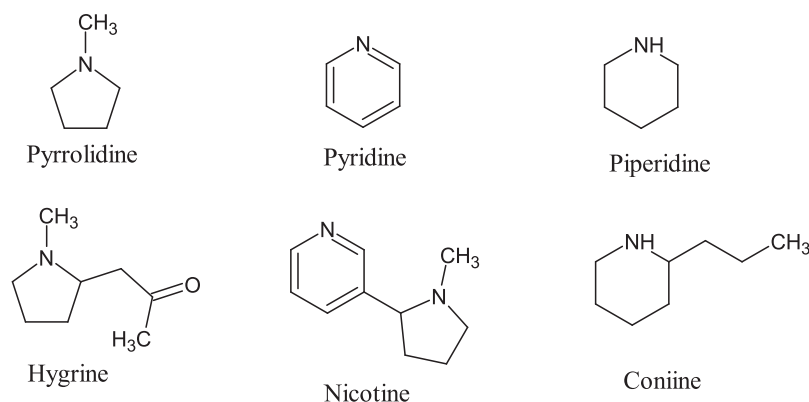


Figure 9.—Examples of alkaloids with main structural types.

has a competitive antagonistic effect on adrenergic receptors and causes strong psychic stimulation, an intensification of sexual emotions, a slight change in perceptions that can cause weak hallucinations, and sometimes spontaneous erections in males (Aubry 2012).

Fields of application of extractives

There are many possibilities for recovering wood extractives, which could then be used in the fields of pharmacology, perfumery, cosmetics, agrifood, agriculture (Mounguengui 2008, Huang et al. 2009). In the rest of the work, we mainly address the areas of application that have aroused interest in recent decades.

Food industry

Lipid foods are less resistant to oxygen oxidation during storage. Lipid oxidation is the major cause of deterioration of foods containing fat, and such foods must be preserved with antioxidants. An antioxidant can be defined according to Halliwell (1994) as an entity that, present in low concentration, can reduce, delay, or prevent oxidative destruction of biomolecules. The antioxidant activity can be evaluated by several methods: ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)) or TEAC (Trolox equivalent antioxidant capacity) test (Miller et al. 1993); ORAC (oxygen radical absorbance capacity) test (Glazer et al. 1993); DPPH (2,2-diphenyl-1-picrylhydrazyl radical) test (Brand-Williams et al. 1995); Methyl linoleate test; FRAP (ferric reducing antioxidant power) test (Benzie and Strain 1999). Antioxidants can be provided naturally by food (fruits, vegetables, tea, red wine, coffee, and cocoa). However, in the food industry the synthetic antioxidants officially authorized and used—namely Butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tertiary butyl hydroquinone (TBHQ), and propyl gallate (PG) (Branen 1975)—are carcinogenic and accumulate in the body (Linderschmidt et al. 1986, Kalamouni 2010). When confronted with this problem of toxicity of synthetic antioxidants, less toxic sources of natural antioxidants would be a better alternative. Among the natural antioxidants, we can cite the phenolic compounds that are found in almost all plants, which can stop the exponential development of lipid radicals to form stable phenolic radicals while breaking the oxidation chain reactions (Diouf 2003). Many publications describe natural antioxidants (Pietta 2000, Moure et al. 2001). These natural compounds are already finding their applications in the food industry, we can cite, e.g., the case of ascorbic acid (vitamin C), tocopherol (related to vitamin E), sesame oil, and olive oil (Taga et al. 1984, Altarejos et al. 2005, Pérez-Bonilla et al. 2006, Kalamouni 2010). Anthocyanins are widely used in the food industry and cosmetics because of their coloring properties and their ability to trap free radicals.

Agriculture

In addition to their antioxidant properties, wood waste extracts can also have several applications, such as fungicide, fungistatic, insecticide, nematocide, herbicide, bactericide, bacteriostatic; hence, there is growing interest in using wood wastes in agriculture via the extractives contained therein. Lall et al. (2006) found that sitosterols have good inhibitory activity against *Aspergillus niger*, *Cladosporium cladosporioides*, and *Phytophthora* sp. fung.

Pterocarpanes are flavonoids with good antifeedant activity and could be used in agriculture for protection against pests. The antifungal activity of plant sitosterol has been demonstrated by Mbambo et al. (2012). The biocidal particularity of certain terpenes such as resin acids or tropolones has biocidal properties (Roussel-Boustia 2000), which could be used in agriculture for protection against pests. Unlike organophosphorus or organochlorine biocides used in agriculture, which have persistent and dangerous harmful effects on human health, greener alternatives to these carcinogenic compounds would be a huge step forward in protecting the environment and consumer health. Several authors have shown that initially durable wood becomes more susceptible to lignivorous fungi or termites after undergoing extraction treatments with organic and/or aqueous solvents (Oliveira et al. 2010, Kirker et al. 2013). This fragility of the wood after extracting the extractives contained therein would facilitate faster degradation of wood waste in the environment and would make it less risky to use as compost in agriculture.

Pharmaceutical

Phytosterols (β -Sitosterol, stigmasterol) present in the wood of *Coula edulis* are very important molecules that are part of the sterol family (Lercker and Rodriguez-Estrada 2000). These molecules have important biological properties. Phytosterols are biogenetically and structurally close to steroids, which are biologically active. Numerous studies have shown that sterols and triterpene alcohols have anticancer properties on colon, lung, and prostate cancer (Raicht et al. 1980, Smith et al. 1996, Awad et al. 2004, Woyengo et al. 2009). Stigmasterol has antidiabetic, anticancer, antidiarrheal, and antiviral properties (Venkata et al. 2012). Moreover, sitosterol is the compound that best represents phytosterols, belonging to the class of sterol molecules (Liswidowati et al. 2001). Hydroxymatairesinol, an extract present from Norway spruce (*Picea abies*) knots, is used as a food supplement for the fight against breast cancer and in treatment of the prostate (Stevanovic and Perrin 2009). In pharmacy and nutraceuticals, aspirin, which is a derivative of salicylic acid extracted from willow bark (*Salix* sp.), is used as an antipyretic, anti-inflammatory, analgesic, and anticoagulant. Triterpenes such as lupeol, botulin, and betulinic acid extracted from the bark of yellow and white birch are used for their anticancer activities. Ginkgo extract (*Ginkgo biloba*) is rich in polyphenols and is very effective against memory disorders, peripheral vascular deficiencies, muscle degeneration, tinnitus, vertigo, and diabetic retinopathy (Qa'dan et al. 2010). Extracted from the bark of cinchona, quinine is used in pharmacies as an antimalarial. Taxol was isolated from the bark of the Pacific yew (*Taxus brevifolia*) in the 1970s, and is used for its anticancer properties. Secondary metabolites from natural products are potential sources of acetylcholinesterase inhibitors, which are key enzymes in the treatment of many neurodegenerative diseases. Reported activities of *Beilschmiedia insignis* alkaloids showed that the five aporphine alkaloids, namely isocorydine (1), norisocorydine (2), (+)-laurotetanine (3), (+)-N-methyl-laurotetanine (4), and (+)-boldine (5), exhibit acetylcholinesterase inhibitory activities with percent inhibition values ranging from 44.9 to 74.5 percent (Wan Mohd et al. 2021).

Cosmetic

Linalool and santalol extracted from rosewood (*Aniba duckei*: Lauraceae) and sandalwood (*Santalum album*: Santalaceae), respectively, are used for perfumes in cosmetics. The composition of make-up products is often noted because, in addition to certain products that benefit from organic certifications, make-up is essentially based on synthetic ingredients such as silicones, talc, and dyes. The coloring and natural origins of certain wood extractives could make them useful as alternatives to the synthetic dyes used in the composition of make-up products.

Industrial

Among all the extractives, the most studied and those that often find industrial applications are polyphenols (Stevanovic and Perrin 2009, Fernandez-Agullo et al. 2015). For years, tannins have been used to make green adhesives, flame-retardant foams, dyes, and for tanning leather. In the rubber tree (*Castilla elastica*), the extracts (polyterpenes) make it possible to obtain the latex for the manufacture of natural rubber (Stevanovic 2011). Extract of balsam fir (*Abies balsamea*) containing juvabione is used for inhibition of beetle juvenile hormone. Some species have extractives that inhibit the growth of wood weathering agents (bacteria, termites, and fungi; Maranhão et al. 2013), and teak wood contains large amounts of quinones responsible for durability natural to this wood. The extract of this essence inhibits the growth of *Trametes versicolor* (white rot fungi) at concentrations of 58 mg/mL (Niamké et al. 2012).

Interest of wood waste

Côte d'Ivoire is a timber-producing and -exporting country. Côte d'Ivoire exported 315,114.948 m³ of wood according to the 2017 activity report of the Department of Forest Production and Industry (DPIF 2017) of the Ministry of Water and Forests. In Côte d'Ivoire, 387 Forest Exploitation Perimeters (PEF) are defined, constituting the rural domain, and covering an area of approximately 14,210,096 ha (44 percent of the national territory), for a theoretical annual exploitation quota estimated at 3,553,846.15 m³. During 2017, of the 387 existing PEFs, 377 PEFs were allocated, of which 365 (97%) were authorized for operation. The volumes of wood taken from these logging perimeters (Table 1), from primary processing

Table 1.—Average volume of wood harvested per Forest Exploitation Perimeters (PEF) calculated by Initiatives for Community Development and Forest Conservation (IDEF) based on figures from the 2016 Department of Forest Production and Industry (DPIF) report.

Forest regions	Volumes (m ³)	No. of PEFs in operation	Average volume taken per PEF (m ³)
Bondoukou	111,249.793	12	9,270.812
Yamoussoukro	292,840.412	39	7,508.128
Bouake	58,169.043	8	7,271.130
Seguela	15,939.05	3	5,313.016
Abidjan	163,447.342	35	466.981
Man	215,671.725	44	4,901.630
Daloa	116,703.599	25	4,668.143
Gagnoa	128,438.659	30	4,281.288
Abengourou	64,716.481	19	3,406.130
San-Pedro	37,046.369	15	2,469.757

companies (e.g., felling, sawing, slicing, peeling) to third-level processing companies (e.g., carpentry), generate wood residues that have no value for these companies and are abandoned in our environment as waste. This wood waste is available in large quantities in our environments and is a great source of bioactive molecules that we could extract and recover upstream before any energy recovery as biofuels, with the aim of replacing petrochemical products as shown by numerous studies (Fernandez-Agullo et al. 2015, Meullemiestre et al. 2016, Bostyn et al. 2018, Santos et al. 2019, Das et al. 2020, Zhou et al. 2020, Zwingelstein et al. 2020). Taking account of extractives molecules in wood waste would add value to this waste, thus making it possible to regulate certain aspects of insalubrity by reducing environmental pollution. This would also make it possible to reduce the pressure on very resistant, highly prized noble species by giving durability to species that are less valuable, or those that are impregnable and not very durable (Onuorah 2000, Brocco et al. 2017, Mbakidi-Ngouaby et al. 2018, Kadir and Hale 2019, Eller et al. 2020, Kadir and Hassan 2020, Wu et al. 2020, Zulfikar et al. 2020). Thus, wood waste constituting the end of life for forest industry products could be the raw material of a so-called extractives sector, very little explored, thus inducing a circular economy with value chains. The stakes are high and will ultimately lead to a reduction in the environmental impact of forestry activity (Wang et al. 2011, Wen et al. 2019).

Conclusion

Wood contains extractives compounds, the quantity of which varies from one tree to another and from one region to another and according to the age of the tree. These extractives can be extracted by suitable techniques and solvents. They are natural and have chemical and biological properties that can be exploited and have been exploited to date in various fields and sectors of activity. The availability of wood waste in developing countries whose economy is largely based on agriculture, such as Côte d'Ivoire, is an opportunity for its development in view of the varied content and composition of extractives from this waste. The multiple possible uses known to date and the renewable and natural nature of this resource are attracting more interest from researchers. The establishment of an “extractives” sector would be interesting especially because it would be an added value for logging on the one hand, and on the other hand would ensure better management of forests and contribute to stronger environmental resilience.

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