

REVIEW: THE VALUE OF WOOD EXTRACTIVES FROM *PINUS RADIATA*

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SUMMARY

The wood extractives from softwood species, which include resin acids, fatty acids and triglycerides, have useful properties making them valuable as natural products. Their water repellency, adhesive properties and biological activity make them useful in manufacturing, agriculture and medicine with broader applications expected to be developed in the future with a shift toward renewable resources. These wood extractives can be problematic in paper manufacture as they cause deposits on machinery and in the paper products, which requires higher levels of maintenance, limits water recycling, increases wastewater toxicity and can reduce product quality. Current methods for addressing these problems in thermo-mechanical pulp (TMP) and paper mills include treatment of wood to reduce extractives content prior to pulping, tighter control of processes to prevent formation of deposits, and the use of additives to fix extractives into the paper product. Recovery of the wood extractives from the process water in a reasonably pure form would provide new value-added products turning a once troublesome material into something of value for existing pulp and paper mills.

Keywords: Wood resins, natural products, softwoods, thermo-mechanical pulp, bioactivity

INTRODUCTION

The term wood extractives can include many different compounds that are extractable from wood by a variety of methods. In this review paper the term is used to describe those lipophilic wood extractives that are released into process waters during thermo-mechanical pulping of softwoods. These extractives can also be extracted from wood using organic solvents. The wood extractives originate in parenchyma wood cells and resin canals and are produced by the plant for various purposes (1). They make up only a few percent of the total dry wood weight, although different parts of the tree and different species contain different amounts and composition of extractives, with a clear contrast between the extractives from softwood and hardwood species (1). Softwood is derived from conifer species which are commonly called pines or spruces. They share characteristics with their ancestors believed to be widespread during the Triassic period more than 200 million years ago, whereas hardwood is derived from flowering trees or angiosperms, which are believed to be evolved later during the early Cretaceous period (2).

Radiata pine or *Pinus radiata* is a softwood tree native to the central coast of California in the USA and two small islands off the Mexican coast (2). It is a fast growing, medium density softwood that has been cultivated for over one hundred years. Though now under threat in its native location, it is a common plantation species in the southern hemisphere, used for paper production (2). Norske Skog's paper mills in Australia and New Zealand process predominantly *P. radiata* wood (3).

Properties Of Wood Extractives

The wood extractives released by thermo-mechanical pulping of softwood species can be categorised into three major classes of compounds: resin acids, fatty acids and triglycerides (4). Example structures of these classes are given in Figure 1. In addition, there are also small amounts of various other compounds including sterols, sterol esters and waxes. A volatile component containing monoterpenes is largely lost to the atmosphere during wood pulping (4). Hydrophilic or water-soluble compounds such as soluble carbohydrates and salts are also released during pulping but they are not generally classed as wood extractives as they are not extracted by organic solvents.

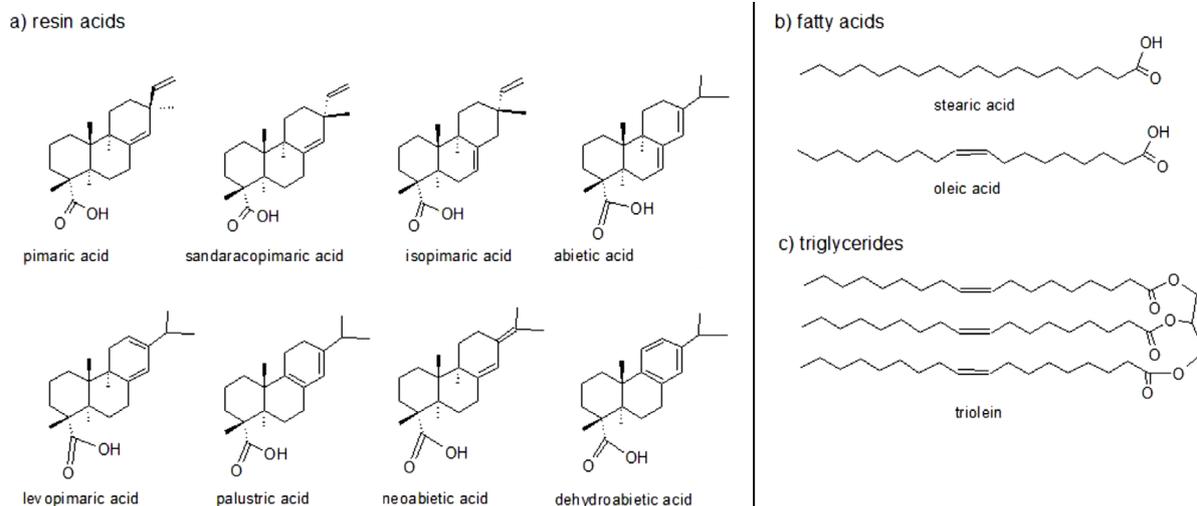


Fig. 1 Structures of resin acids, fatty acids and triglycerides.

The resin acids are classed as diterpenes meaning that they are produced in the plant by linkage of 4 isoprene units (1). They are found in the oleoresin which is produced by conifer species as a defence against bark boring beetles and the harmful fungi they carry (5, 6). When the thick, sticky oleoresin mixture is secreted by the tree, it engulfs the attacking beetles and their fungal pathogens, killing them and impeding their attack. The volatile monoterpene component of the oleoresin evaporates, and the remaining resin acid component hardens to form a physical barrier that seals the wound in the tree and prevents further attack (7). Structures of the eight most abundant resin acids in softwoods (4, 8) are shown in Figure 1 a). These can be divided into two groups based on their chemical structure. Firstly, the pimarane type resin acids in the first row which have a vinyl group attached at position C-13 and secondly, the abietane type resin acids, which have either an isopropyl or isoprenyl group in that position. The structure of different resin acids also results in differences in solubility. The pimarane type are less soluble than the abietate type resin acids and dehydroabietic acid is the most soluble due to the concentration of electrons around its aromatic ring which make the structure more polar (9). A variety of fatty acids and triglycerides which originate in the parenchyma cells in wood also make up a portion of the wood extractives. Some example structures are shown in Figure 1 b) and c). Triglycerides are natural fats or oils that consist of three fatty acid molecules bonded to glycerol via ester bonds forming a single molecule. Oleic acid is the most abundant fatty acid in softwoods and triolein is the most abundant triglyceride (1, 8).

The resin acids and fatty acids are organic acids having the carboxylic acid group -COOH . This makes them weak acids as the hydrogen in the carboxylic acid group can dissociate in water to produce a positively charged hydrogen cation and a negatively charged anion (10).

Resin and fatty acids and their anions are also surface active (also called surfactants) having in their structure a polar segment and a nonpolar segment (4) as depicted in Figure 2 a). The carboxylic acid group is polar, and upon dissociation is even more polar, whereas the molecule or anion body is nonpolar. Thus, the acids or anions adsorb at polar/non-polar interfaces including the air-water interface, colloid surface and on surfaces in contact with water. An important property of surfactants is their ability to form micelles in solution. Micelles are structures formed by groups of surfactant molecules arranged such that the hydrocarbon ends form a hydrophobic core and the solvated polar groups form an outer core as depicted in Figure 2 c). Micelles can form from a single species or from a mixture of surfactants. They can also solubilise hydrophobic substances by absorbing them into their core (4).

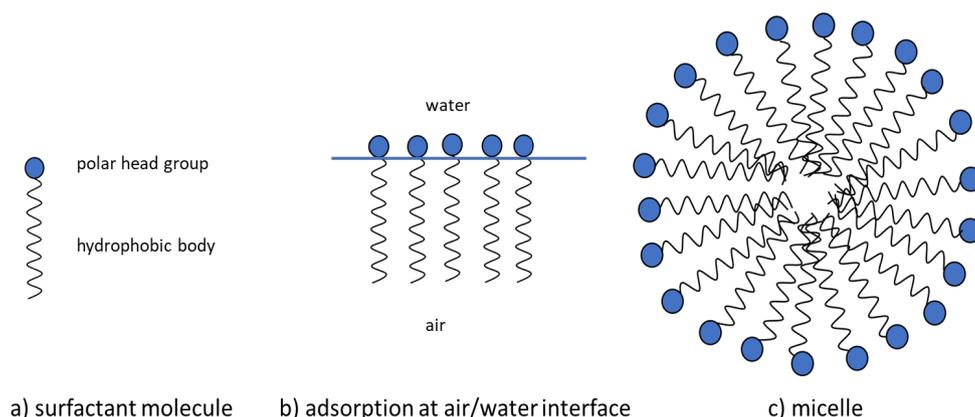


Fig. 2. Surfactant structures

Triglycerides, in contrast to organic acids, have no labile hydrogen atoms (4). As such, they remain as neutral molecules regardless of pH and have very limited solubility in water. They are also not surface active. Being nonpolar molecules, they are soluble in nonpolar solvents such as hydrocarbons and other fats or oils and can also be absorbed into resin and fatty acid micelles. Triglycerides hydrolyse under alkaline conditions to form free fatty acids. They can also hydrolyse under the action of lipase enzymes. During wood storage conditions the triglycerides in the wood produce free fatty acids which can affect the composition of wood extractives (4).

The wood extractives found in different softwood species are similar, however, *P. radiata* is known to have a higher proportion of resin acids in comparison with the more extensively researched *Picea abies* (Norwegian spruce), which is the major northern hemisphere species used for paper production (11, 12). The comparison of extractives components in wood pulp from these two species is presented in Table 1 which shows that *P. radiata* TMP contains roughly double the weight of resin acids and roughly half the weight of triglycerides.

Table 1: Extractives in *P. radiata* TMP compared to *P. abies* TMP

	<i>P. abies</i> TMP	<i>P. radiata</i> TMP
resin acids (g/kg)	2.00	4.55 ±1.02
fatty acids (g/kg)	0.40	0.50 ±0.18
triglycerides (g/kg)	4.55	1.49 ±0.33
reference	(12)	(11)

The wood extractives in the process water form spherical particles around 0.1 -3 µm in diameter (4, 13). Research has shown that their structure consists of a hydrophobic core containing triglycerides and other neutral compounds surrounded by an outer shell containing the more polar compounds such as resin and fatty acids (14, 15). This structure is depicted in Figure 3. The nonpolar sections of the resin and fatty acid molecules embed beneath the colloid surface with the polar carboxylic acid group at the surface, oriented toward the water phase. Research by Lee et al. suggests that in *P. radiata* wood extractive colloids, the fatty acids form a mobile intermediary shell between the surface shell and the core (16). The location of the fatty acid shell was found to change with the proportion of triglycerides. At low triglyceride levels the fatty acids were drawn into the core, while at high triglyceride levels they were pushed towards the surface (16). *P. radiata* has a much higher resin acid component than does *P. abies* on which previous studies were based which may explain this behaviour.

Problems With Wood Extractives In Papermaking

In paper manufacture world-wide, water-immiscible wood extractives can cause significant problems (4, 17-20). Wood extractives are released from the wood cells and resin canals, where they are naturally found (1), into the process water during the pulping process. Being lipophilic they form colloidal particles which are suspended in the process water or adhere to the papermaking fibres. Their presence can cause detrimental effects throughout paper production and printing processes which include pitch deposits, reduced paper quality, runnability problems for printing machines, limiting water saving measures and toxicity of waste waters. These problems are more pronounced for thermo-mechanical pulp (TMP) mills that process wood species high in extractives such as Norske Skog's mills in Australia and New Zealand which use *P. radiata*

wood (11). A variety of methods are implemented in pulp and paper mills to reduce and manage the problems caused by wood extractives (4, 18, 19). They include pre-treatment of wood, process control to prevent deposits, the use of additives that fix extractives into the product, and biological treatment of effluent waters.

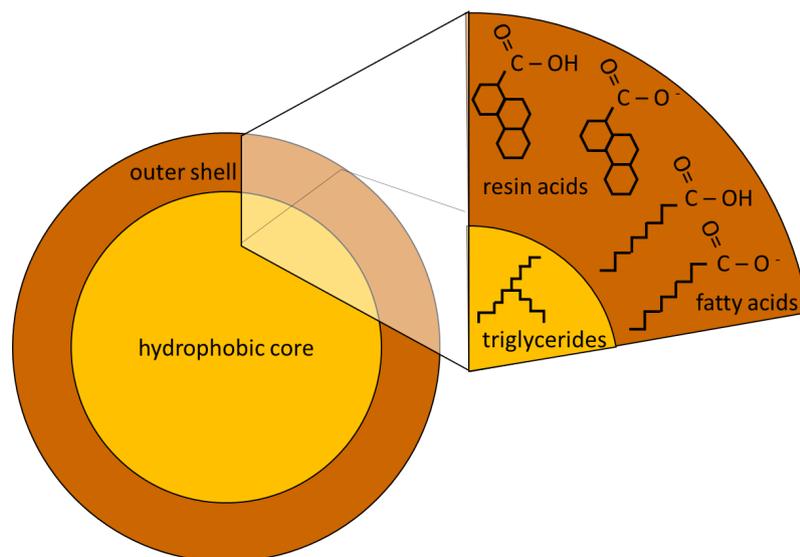


Fig. 3. Wood extractive colloid structure

Pitch deposits occur on machinery when the colloidal suspension of wood extractives formed during pulping is destabilised, causing the colloids to aggregate and deposit (19). The composition of pitch deposits has been analysed, as have the factors that contribute to colloidal instability. These factors include temperature and pH (12, 20-26), shear (23), extractives composition (15, 22, 26, 27), ionic strength and calcium ions (21, 23, 26, 28-30) as well as dissolved organic substances originating from the hemicelluloses and pectins (13, 27, 31-36). Extensive research has been undertaken over the past decades by several research groups including Abo Academi in Finland and the University of Tasmania in Australia to study wood extractives from softwoods and the causes of pitch deposition.

A study of deposits on machinery in Norske Skog's New Zealand and Australian paper mills in 2008 revealed high levels of wood extractives including fatty acids, glycerides and particularly resin acids and resin acid salts in the deposits (37). Deposition was correlated to extractive levels measured in process water (37). At one location, high fibre-bound extractives were identified as the major cause of deposits and at another, inefficient mixing of soda ash for pH control caused dissolution of resin acids and subsequent formation of insoluble aluminium resinates (37). In both cases the problems were then able to be managed to prevent severe deposition. Further research into causes of pitch deposition at Norske Skog's Albury mill identified important factors in colloidal stability (38). Soluble calcium, shear forces and downward temperature shock all destabilised colloids. Dissolved organic wood polymers and pH were also important. A parameter named the ester to acid ratio (EAR) was identified which helped to explain the observed seasonal pattern of pitch depositions (38). The EAR was defined as the ratio of glycerides (of fatty acids) to free fatty and resin acids. In summer months when the EAR was lower, pitch deposition worsened. A lower EAR coincides with lower triglyceride levels in the colloid compared to the ratio of resin acid and fatty acid. This has been found to

affect the structure of the pitch colloid (16) and result in a migration of fatty acids away from the surface of the colloid to the interior leading to a less stable colloid (16,38).

Paper product quality is affected by increased wood extractives in the pulp, and by deposits occurring in the paper machines and on the paper (4). Wood extractives incorporated in paper reduces its strength by limiting hydrogen bonding between cellulose fibres. Deposits in paper can cause visible specks or variations in thickness and deposits on machinery can produce holes or imprints in the paper. Resin acids in paper used for food packaging is of concern as they have been shown to be toxic to human cells (39), although, the levels that migrate into food products has been shown to be well below the recommended exposure limit (40). Resin acids are also responsible for contact allergies to wood products including paper from thermo-mechanical pulp (TMP) (40).

Excess levels of wood extractives in paper can also cause problems for printing presses. The presence of extractives changes the chemistry of the paper surface inhibiting bonding of glues and printing inks (4). Deposits of extractives can also occur on printing press rolls, causing holes and printing defects (4).

Water saving measures in pulp and paper mills are limited by the presence of wood extractives because closure of process water circuits allows the extractives to accumulate (18, 19). At Norske Skog's mills in Australia and New Zealand, problems related to deposits have been exacerbated in recent years by increased closure of process water circuits to reduce consumption of fresh water resources in-line with best practice manufacturing principles (38, 41). In Australia there is increasing pressure to reduce freshwater consumption especially in drier locations such as Albury where one of Norske Skog's mills is located (42).

Wood extractives, and particularly the resin acids are a major contributor to the toxicity of TMP effluent (4). Resin acids are toxic to aquatic life including fish and plankton (9). The extractives must therefore be removed from wastewaters. Treatment is commonly achieved aerobically by biological degradation (4, 43).

Various strategies have been employed in pulp and paper mills to reduce these problems. Improved understanding of colloidal stability and increased process automation has enabled tight control over processes to prevent conditions that destabilise colloids which can reduce pitch deposits (4). The process water pH can be used as a tool for minimising pitch deposits (38). Deposition of pitch is more likely to occur under acidic conditions and pH's close to 6-7 are generally found to be optimum. This pH region is close to the pK_a of the various resin acids, the major component in the wood extractives of *P.radiata*. The use of additives is also common in preventing pitch deposition. Mineral adsorbents such as talc, bentonite, and kaolin can fix extractives into the paper product thus removing them from the system. Additives that cause agglomeration such as aluminium compounds can also be used to increase the effectiveness of adsorbents (19). Cationic polymers called retention aids are also used which flocculate extractives particles or colloids, so they are fixed into the paper product (4, 18, 19). However, disadvantages of these treatments are the cost of additives and changes to paper properties with incorporation of extractives and additives. Alternatively, the wood extractives content of wood chips can be reduced before pulping by mechanical compressive pre-treatment (44) or enzyme treatment (45) thus reducing problems in down-stream processes. Most of these current approaches to managing wood extractives in TMP mills do not allow for recovery of the extractives as they are either subject to biological decomposition, fixed in the paper product or collected in waste water.

Potential Uses For Wood Extractives

The natural properties of wood extractives that protect the tree from insect and microbe threats also make them useful for a variety of human purposes. Their physical properties of water repellency and tackiness make them useful for waterproofing timber (46) and as additives in adhesives and rubber. Their chemical properties and biological activity against fungal and insect pathogens can be useful in medicine, agriculture and treatment of building materials (47-57). Some of these properties can even be improved upon by using wood extractives as starting materials for synthesis of more active derivatives (56, 57). Wood extractives can also be a source of organic molecules for more general chemical synthesis of a wider variety of compounds (58). These useful properties of wood extractives have been exploited in different ways throughout human history (5). The development of new methods and knowledge of wood extractives may provide an important and sustainable source of materials for a variety of purposes into the future (6).

Historically, oleoresin from conifer species was a major industry supplying pitch and tar for waterproofing of wooden sailing ships, as well as turpentine produced from the volatile component (1, 5). As the era of wooden ships passed, there was no longer such a need for waterproofing timber. The rise in petroleum production also provided a new resource for solvents, fuels and chemicals that could be obtained more cheaply. However, oleoresin is still produced commercially by extraction from wood and bark or by tapping live trees (6). The crude oleoresin is refined by steam distillation into gum turpentine containing the volatile monoterpenes, and gum rosin containing the diterpenoids. Turpentine is used as a solvent and rosin goes into the manufacture of a wide range of products including adhesives, additives to rubber products, printing inks and paper sizing (5, 6, 59). The global gum-rosin market is expected to reach USD 2.49 billion by 2024 with increasing demand for higher grade product (60, 61). There is however, a trend toward substitution of gum rosin with rosin derived from tall oil (58). Tall oil is a by-product of the Kraft or sulphate process which is a widely used chemical pulping process that produces high quality cellulose pulp (62). Crude tall oil is separated into fatty acids and resin acids (rosin). Recovery of the tall oil not only provides the industry with a valuable by-product but reduces problems caused by wood extractives remaining in circulating process streams. These problems include reduction of process efficiency, scaling in evaporators, fouling of boilers, increased emissions and increased effluent toxicity (62). The applications for tall oil rosin are limited, however, due to contamination with sulphur compounds which give the product an unpleasant odour and darker colour (63, 64). Thus, purification is necessary to produce a higher grade product. Thermo-mechanical pulping does not involve the use of sulphur compounds and is therefore a cleaner source of wood extractives with the potential to supply the existing market and developing new markets.

There has been renewed interest in wood extractives for wood treatments. Chemically benign treatments for timber are sought, particularly for use in decking, fencing and playground equipment where it is undesirable to use chemical treatments that might be harmful to people or the environment (46-48). Mixtures containing wood extractives have been studied and found to be beneficial. Dahlen et al. (46) used resin acids from tall oil to treat decking boards and found that they provided water repellency for up to two years which reduced absorption of water by a third and splitting of the timber by a half. Temiz et al. (47) studied resin acid mixtures in combination with boric acid which is a less toxic wood preservative than arsenic or chromium but is prone to leaching due to its high solubility in water. Wood extractives, particularly resin acids in combination with boric acid provided protection against fungal rot and prevented leaching of the boric acid (47). Likewise, Hien et al. (48) demonstrated the benefit of resin acids as a fixative for copper sulphate. The addition of the resin acids reduced leaching of the copper by half and reduced fungal decay

(48). As effective wood treatments utilising wood extractives are developed, and an awareness of the need for environmentally benign wood treatments grows, a larger market for wood extractives may also grow.

Wood extractives have value in medicine due to their bioactivity. Oleoresin has been used traditionally around the world as a medicine to treat wounds and infections. For example, in Lapland, Northern Finland, for centuries people have boiled oleoresin from *P. abies* with butter or animal fat to produce a salve used to treat wounds and skin infections (53). In Turkey, oleoresin from the native *Pinus brutia* is used in traditional medicines to treat stomach complaints, skin wounds and infections, and to clean the mouth and teeth (52). More recently, in the search for new bioactive compounds for pharmaceutical and agricultural industries, the activity of individual compounds has been studied. This has revealed many examples of effective activity that justifies those traditional remedies (7). Soderberg et al. (50) studied the antibacterial activity of rosin from tall oil and individual resin acids and found activity against Gram-positive bacteria but not Gram-negative bacteria. Greater activity was found in the abietic type resin acids with the most active being dehydroabietic acid (50). Increasing drug resistance in human pathogens is driving increased interest in developing new antibiotic drugs. Antibiotic activity of resin acids against drug-resistant strains of human opportunistic pathogens have been reported. Isopimaric acid isolated from *Pinus nigra* cones was shown by Smith et al. to have activity against multi drug-resistant and methicillin-resistant strains of *Staphylococcus aureus* (51). Dehydroabietic acid isolated from resin oil from *Pinus elliotii* was shown by Leandro et al. to be active against drug resistant *Staphylococcus epidermidis* (55). Derivatives of resin acids can exhibit an even wider range of activities making them ideal starting materials for synthesis of a broader range of drugs. For example, Fonseca et al. reported antiviral activity of dehydroabietic acid derivatives (55) and Gigante et al. reported antiviral and anticancer activity of abietic acid derivatives (56). Anti-inflammatory and anti-protazoal activity have also been recently reported for derivatives of levopimaric and dehydroabietic acid respectively (49, 54).

CONCLUSIONS

There is a need for renewable sources of organic chemicals to replace the finite fossil sources of hydrocarbons, from which most modern chemicals are derived. Wood is a renewable resource when grown and managed sustainably. Thus, wood extractives may be a valuable alternative source of organic chemicals. James H. Clarke, a leading researcher in green chemistry, identifies waste materials from food and manufacturing as valuable future sources of chemicals (65). He argues that to achieve a stable and sustainable economy, society must recognise and look toward these opportunities. Currently, wood extractives are a waste material from thermo-mechanical pulping that cause problems in the processing of wood fibre and must be treated by biodegradation before they can be discarded. Alternatively, recovery of these extractives may provide high grade products for current and new industries that develop in a shift to a circular economy.

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