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Chemicals from Wood

T Elder, USDA – Forest Service, Pineville, LA, USA

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Introduction

A wide array of both commodity and specialty chemicals can be derived from wood, either as a primary product or by-product of another process. The technologies in which chemicals are the primary products include thermal degradation, hydrolysis/fermentation, direct collection, and extraction methods. Chemicals collected as by-products generally come from fiber-producing processes, including pulp and paper and steam explosion. While cellulose, lignin, and derivatives thereof could be classified as chemicals derived from wood, the current review will be limited to low-molecular-weight chemicals from wood. The synthesis and utilization of various chemicals from renewable resources have received considerable recent attention through research efforts in green chemistry.

Extractives

Perhaps the oldest of the chemicals produced from wood are those derived from the extractives. The term ‘naval stores’ provides a clue to the waterproofing applications for which these chemicals were originally used. The extractives can broadly be divided into terpenes, resin acids, and fatty acids.

Terpenes

Terpenes are relatively volatile hydrocarbons based on isoprene (2-methyl-butadiene) units, and are the major components of turpentine. Turpentine was once produced largely by tapping trees and collecting the exudates, which after processing are called ‘wood naval stores.’ Currently, most turpentine comes from the sulfate pulping process, in which the volatile materials are removed by the action of heat and pressure in the digestion step. The volatiles consist

mainly of the monoterpenes, α -pinene, β -pinene, and Δ^3 -carene, depending on the wood species (Figure 1). While turpentine was once used extensively as an industrial solvent, the monoterpenes are now modified into much more valuable products, used in perfumery, flavorings, and to some extent insecticides and disinfectants. Although most terpenes are now produced as a by-product of the pulping industry, the exception to this generalization is natural rubber production. Natural rubber (*cis*-1,4-polyisoprene) comes from *Hevea brasiliensis*, and is still collected by tapping living trees and collecting the latex sap.

Resin Acids

The resin acids, the main components of rosin, are diterpenoids such as abietic acid, neoabietic acid, palustric acid, pimaric acid, and isopimaric acid (Figure 2). Rosins can be isolated from directly collected oleoresins, but are now more commonly separated from tall oil as a by-product of the kraft, black liquor recovery process. Metallic salts and esters of resin acids are used as additives to printing inks to improve gloss, mechanical stability and resistance to chemicals. Rosins are also extensively used in paper sizing and in rubber manufacture as emulsifiers and tackifiers.

Fatty Acids

In addition to the resin acids, tall oil also contains fatty acids. Given the acidic character of both of these components and the very high pH in kraft black liquor, during the recovery process, the acids are converted to insoluble salts, referred to as soaps, that are skimmed from the concentrated black liquor. The skimmings are acidified to release the acids resulting in crude tall oil (CTO). Resin acids, fatty acids, and any unsaponifiable neutral compounds are separated by vacuum distillation. Among the fatty acids are oleic and linoleic acid. The fatty acids find applications in ore separation, metal working, rubber, as detergents, and as drying agents in finishes.

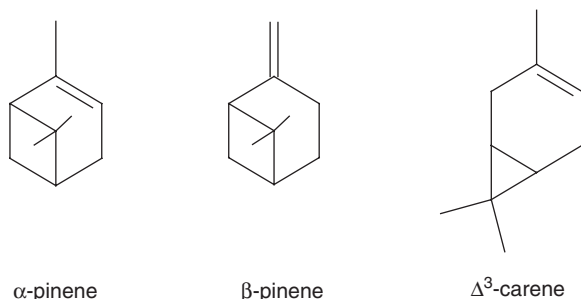
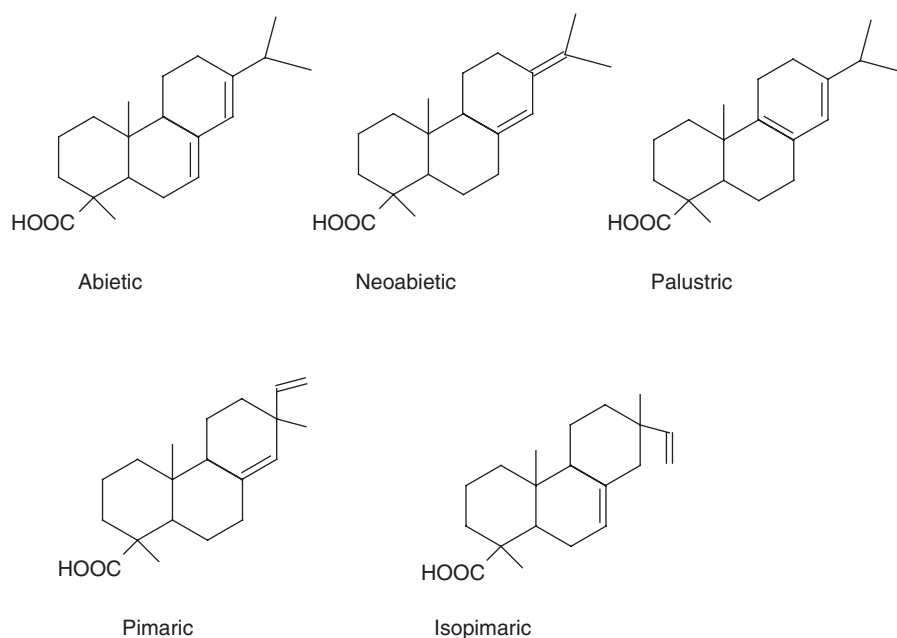
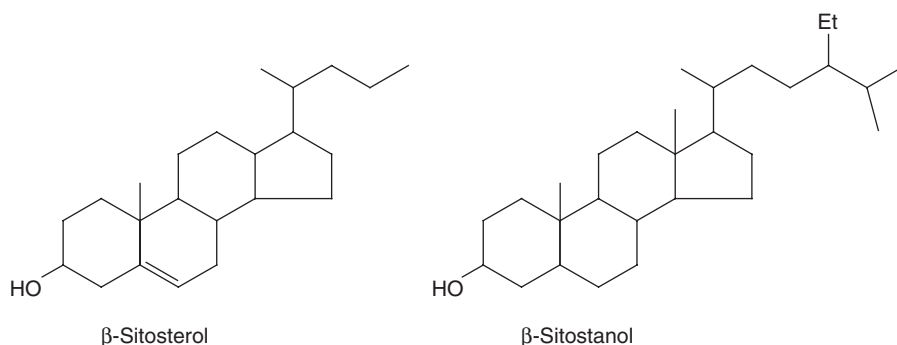


Figure 1 Monoterpenes.

**Figure 2** Resin acids.**Figure 3** Triterpenes.

The neutral fraction of the tall oil is made up of triterpenoid β -sitosterol, β -sitostanol, and lignoceryl alcohol (**Figure 3**). Given the structure of the former compounds, these have been of interest in the synthesis of other steroids that may have biological applications. The butter/margarine substitute Benecol that reduces low-density lipoprotein cholesterol contains sitostanol.

are responsible for the colors in flowers. Tannins, originally used as leather tanning agents, due to their ability to bind to proteins, are represented by the condensed tannins, which are oligomeric flavonoids, and the hydrolyzable tannins that are polymers attached to sugars through ester linkages, which yield gallic and ellagic acid upon hydrolysis. More current applications of the tannins have been as adhesives, antioxidants, and viscosity control agents.

Phenolics

Among the other extractives that are present in wood are a number of phenolics (**Figure 4**). These include the lignans that occur through coupling of C_6C_3 groups, and the stilbenes, made up of 1,2 diphenyl ethylenes. In addition are the flavonoids, and their derivatives, with $C_6C_3C_6$ skeletons. These may be antifungal, can repel insects, act as antioxidants, and

Pharmaceuticals

The extractives from wood and bark have had both a long history and recent success with respect to the isolation of important drugs (**Figure 5**). Perhaps the oldest and best known of these applications is the alkaloid quinine, present in the bark of *Cinchona calisaya*, *C. cussiruba*, *C. legeriana*, and *C. officinalis*.

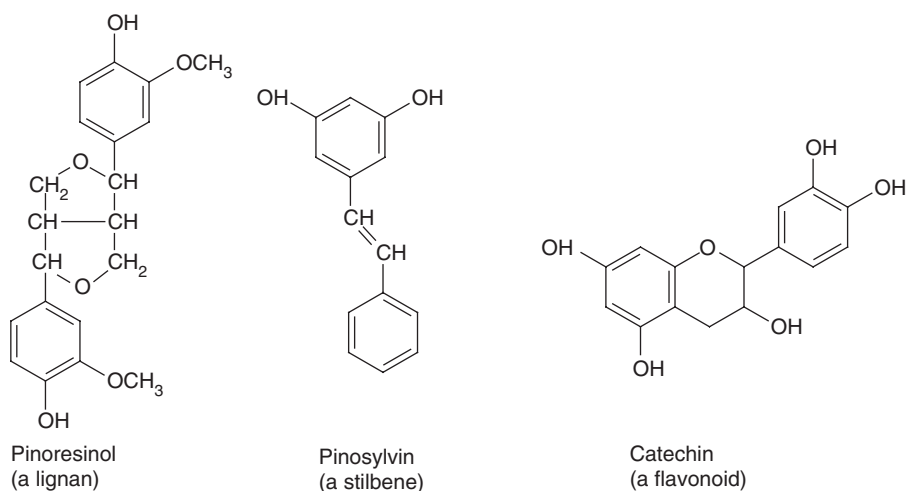


Figure 4 Other extractives.

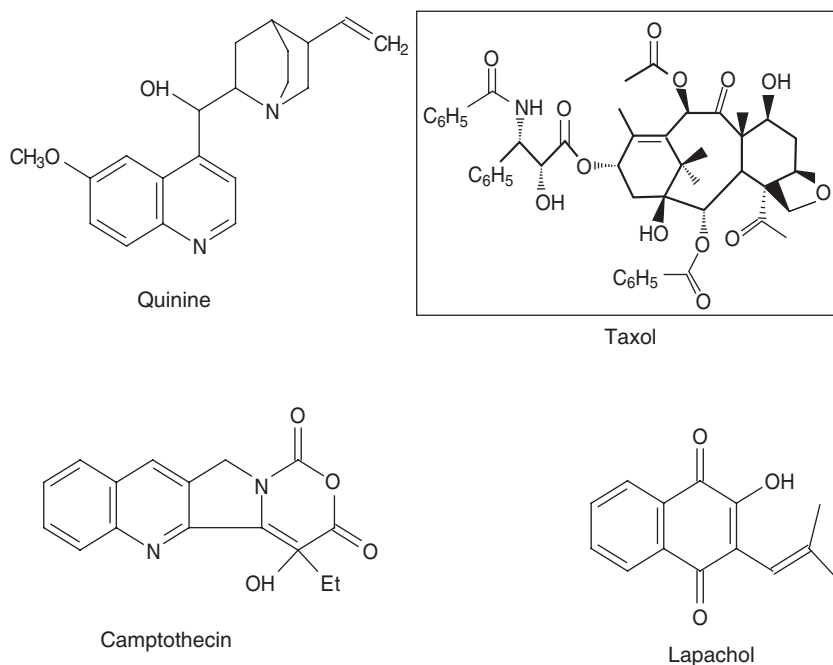


Figure 5 Biologically active extractives from wood and bark.

These trees are native to the Andes and the bark may contain up to 15% quinine. Natives of South America used the bark as medicinal, but it appears that Jesuit missionaries first found that the powdered bark had antimalarial properties. The bark from both the tree and branches is used in a powdered form, and usually taken as an infusion.

A more recent development, of course, is the case of taxol, a diterpene originally isolated from the bark of *Taxus brevifolia*. An extract of pacific yew bark was first found to be effective against rodent cancers in 1962, in 1966 taxol was identified as the active

compound, and in 1971 the structure was published. Taxol is active against leukemias, breast, ovarian, brain, and lung cancers. Limitations in its use have been encountered due to the slow growth, environmental restrictions, and low concentrations of taxol in the bark of Pacific yew. It has been reported that six 100 year-old trees would be required to treat one patient. Recently, several semisynthetic analogs of taxol have been produced from other species of yew.

Camptothecin, an alkaloid isolated from *Camptotheca acuminata* and its analogs topotecan and irinotecan, has been used in the treatment of ovarian

and colorectal cancers. Topotecan has been found to be as effective or more so than taxol in such applications. The tree *C. acuminata*, a member of the Nyssaceae, is native to China and Tibet, where it is known as xi shu ('happy tree'). Harvesting for medicinal purposes caused a rapid decline in the availability, leading to restrictions of cutting and seed exportation. Prior to the exportation bans, plantings were established in the USA, but yields of camptothecin were low. In the meantime, another species, *C. lowreyana*, which is a shrub, has been planted with some degree of success.

Several species of *Tabebuia* (Pau d'Arco), from the rainforests of Central and South America, have been examined as a source of the compound lapachol that has been reported to be effective against some tumor cells. Severe toxicity problems have been reported, however, and to date this compound is not used in cancer therapies.

Polysaccharides

In addition to extractives, polysaccharides have been examined as possible therapeutic agents. A 4-O-methylglucuronoxylan has been isolated from *Fagus crenata* and tested in mice. Cancers in the peritoneal cavity were suppressed, as were the growth rates of tumors. Arabinogalactan, a highly branched, water-soluble hemicellulose with very high molecular weights, that can be isolated from larch heartwood and echinacea, has also received attention from the health care community. This polysaccharide has found use as dietary fiber, for which it is approved, and may have efficacy in immune system responses and as a supplement in cancer treatments. As a dietary supplement, the polysaccharide is rapidly fermented in the intestine, producing short-chain fatty acids that are used by cells in the colon as an energy source. These fatty acids also protect the intestine from diseases and carcinogens. In animal studies, arabinogalactan has been reported to reduce the colonization of the liver by tumor cells.

Lignin

Other by-products from pulping processes are the lignin that is removed during sulfite or sulfate pulping. While most of the sulfate (or kraft) lignin is burned for energy, and as an integral part of the recovery process, the sulfur-containing fractions can be utilized to produce dimethyl sulfoxide (DMSO), dimethyl sulfide, and methyl mercaptan. Methyl mercaptan and dimethyl sulfide are used as odorants in natural gas, while DMSO, due to its solvation properties, is used as a carrier for drugs and

agricultural chemicals. Sulfite lignin, or lignosulfonates, have also been used in chemical applications. Under alkaline hydrolysis or oxidation conditions lignosulfonates will produce vanillin. Vanillin is used as a flavoring agent, upon derivatization can be used in sunscreens and fibers, and is an intermediate in the synthesis of the antiparkinson's drug L-dopamine. Lignosulfonates are also used as viscosity control agents in oil well drilling muds, dust suppressants in paving materials, dispersants, and adhesives.

Hydrolysis and Fermentation

The saccharification of wood for the production of monomeric sugars can be accomplished by several methods, including concentrated acid hydrolysis, dilute acid hydrolysis, and enzymatic hydrolysis. Concentrated acid hydrolysis employs mineral acids (mainly hydrochloric or sulfuric acid) at percentages as high as 80%, such that relatively low reaction temperatures (20–25°C) can be used. The drawbacks to this process involve corrosion of equipment due to the acidic environment, neutralization of the product stream, and recovery of the acid. In the dilute acid process, a two-step reaction is used to maximize the sugar recovery from both cellulose and the hemicelluloses. In the first step, a dilute acid pretreatment is performed (0.7% sulfuric acid, 190°C, 3 min), followed by a hydrolysis step at 0.4% sulfuric acid, 215°C for 3 min. The disadvantage of this method lies in the dilute nature of the product. In order to overcome this limitation, a great deal of engineering work has been reported on varying reactor designs. Enzymatic hydrolysis originally used cellulase enzymes as a substitute for the mineral acid, converting the polysaccharides to simple sugars that would be fermented in a separate step. Subsequently, simultaneous saccharification and fermentation (SSF) methods were developed, in which the cellulase and fermenting microorganisms are combined. The enzymes used in both of these processes have largely been isolated from *Trichoderma reesei*, and can be subdivided into endoglucanases that react randomly along the cellulose chain, exoglucanases that react endwise to produce glucose and cellobiose (a glucose dimer), and β -glucosidases that convert cellobiose to glucose.

Upon hydrolysis, the monosaccharides can be converted to a large number of chemicals via either fermentations or chemical processes. The most familiar of the fermentation methods is the conversion of glucose to ethanol by the action of *Saccharomyces cerevisiae*. More recently pentose sugars, which had been problematic in this regard, have been fermented to ethanol by recombinant

strains of *Zygomonas mobilis*, *Escherichia coli* and *S. cerevisiae*. Acetic acid can be produced by fermentation with *Acetobacter*, or *Clostridium thermoaceticum*, while lactic acid is fermented from glucose by *Lactobacillus*. An acetone–butanol–ethanol blend can be made with an anaerobic *Clostridium*. Acetaldehyde can be produced as a secondary product of ethanol by *Candida utilis* or *Pichia pastoris*, but can also be a direct fermentation product from glucose by either *Z. mobilis* or *S. cerevisiae*. While hydrocarbons are industrially produced from petrochemical sources, it has been found that ethylene, propane, and propylene can all be fermented from sugars by microorganisms. Succinic acid is an important intermediate in the synthesis of butane-diol, tetrahydrofuran, and adipic acid, all of which can also be used in subsequent syntheses. Succinic acid has been successfully produced by the direct conversion of sugars by recombinant *E. coli*.

Another product of fermentation processes is single-cell protein, derived from the dried cells of microorganisms. These may include bacteria, fungi, yeasts, or algae, that produce protein to be used by humans or animals. Sugars in the form of molasses were used as the carbon source for *Torula* yeast (*Candida utilis*) in Germany during World Wars I and II to extend meat supplies. Lignosulfonates, from sulfite pulping, have also been used as the substrate, and lignocellulosic material, upon either enzymatic or acid hydrolysis, has been used to produce simple sugars, used by a number of fungi and yeasts.

The monosaccharides that arise from the acid hydrolysis of cellulose and hemicelluloses can undergo dehydration reactions upon continued exposure to acidic conditions. The products of these reactions are furfural from the pentoses, hydroxymethyl furfural from the hexoses, and levulinic acid (Figure 6). Levulinic acid has recently received considerable attention due to the wide range of potential products that can be derived therefrom. These include ethyl levulinate used as a component in biodiesel fuels, delta-amino levulinic acid (DALA), a biodegradable

herbicide, and 1-4 butanediol for use in polyesters. Hydroxymethyl furfural may be used as an intermediate for plastics, resins, and nylon manufacture. Furfural is used as an industrial solvent and in resin production.

The monosaccharides can also be converted to their corresponding alcohols (alditols) by chemical reduction. Xylitol, mannitol, and sorbitol are used as sweeteners, and sorbitol can be used in the synthesis of ascorbic acid.

The hydrolysis process, in addition to the monosaccharides, produces a lignin residue. While this material can obviously be burned as a fuel, ongoing research is examining its reformation into additives for gasoline. The lignin is initially depolymerized under alkaline conditions and is then subjected to deoxygenation and hydrocracking. These steps convert the lignin polymer into a mixture of hydrocarbons that are proposed as octane enhancers for gasoline.

Thermal Degradation

The production of chemicals from wood by the action of heat includes a broad continuum of processes, varying with respect to conditions and products. In general, these methods are done in the absence of air or other oxidizing agents, such that the substrate is thermally degraded, rather than combusted. The general terms used to describe this process include pyrolysis, liquefaction, and gasification, the latter two selectively producing liquid and gas, respectively, while pyrolysis results in a mixture of all three, the relative amounts of which are a function of the conditions.

Pyrolysis can broadly be divided into conventional pyrolysis and fast pyrolysis. The former encompasses techniques such as carbonization or destructive distillation, while the latter includes flash pyrolysis, rapid pyrolysis, and ultrapyrolysis. In any of these, the process variables are the residence time, temperature, and heating rate.

Probably the oldest of the thermal processes is destructive distillation, occurring under long residence times, on the order of hours to days, slow heating rates, and moderate temperatures (300–500°C). The main product is charcoal, with the liquid phase producing turpentine, pine oil, methanol, acetic acid, and a tar fraction that was originally used in sealing and waterproofing wooden ships. The technology used for this process ranges from a simple pit kiln, in which wood is stacked in a hole in the ground, ignited and covered to limit the amount of air, to industrial-scale furnaces. The charcoal that is produced may be used as either a fuel or a source for

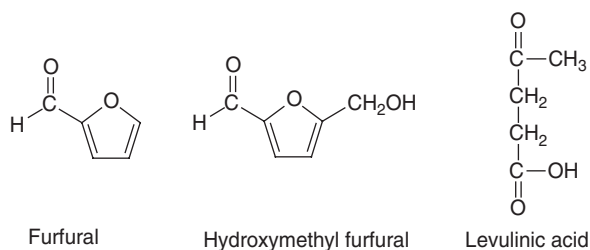


Figure 6 Dehydration products from acid hydrolysis.

activated carbon, that can be applied to filtration and purification processes.

Under shorter residence times, higher levels of the more volatile liquid phase can be collected. The liquid consists of a water-soluble fraction containing methanol, acetic acid, acetone, and relatively low-molecular-weight terpenoids. A heavy insoluble pyrolysis oil or tar is also produced. This is an extremely complex mixture of hundreds of chemical compounds, any one of which is present in limited concentration. The cellulose present will preferentially produce levoglucosan, the hemicelluloses are degraded to furans, while the lignin is represented by a large number of phenolic compounds. These phenolics have been exploited in the proposed utilization of pyrolysis oils in adhesive applications. The gas from conventional pyrolysis is relatively low-energy ($1\text{--}3\text{ MJ kg}^{-1}$) and mainly consists of carbon monoxide and carbon dioxide, with small amounts of hydrogen, methane, and ethane.

Fast pyrolysis is characterized by very short residence times, and very high heating rates, with thermal flux values as high as $3000\text{ cal cm}^{-2}\text{ s}^{-1}$. These conditions quench the reactions, preventing the formation of secondary products. While all three phases can be produced, as a function of process conditions, at the very highest heating rates gaseous products are preferred, with the major component being acetylene. The heating methods by which fast pyrolysis is performed have been varied and novel, including microwave, radiofrequency, and focused solar radiation.

Liquefaction of wood involves treatment at elevated temperatures in the presence of various liquids and catalysts. At relatively high temperatures ($300\text{--}425^\circ\text{C}$) and in the presence of an aqueous solution of sodium carbonate, wood is liquefied at yields as high as 80%. The liquid, which is a complex mixture, can nevertheless be largely composed of phenolic compounds. Alternatively, wood can be liquefied under less severe conditions (temperatures $80\text{--}150^\circ\text{C}$) in the presence of acid catalysts such as hydroiodic, sulfuric, hydrochloric, or phosphoric acids, or simply with solvents, such as phenols, ketones, alcohols, or glycols, at somewhat higher temperatures ($240\text{--}270^\circ\text{C}$). These conditions will convert the wood into a liquid product with a paste-like consistency that has been used in adhesive applications, foams, and molded products.

Gasification, as the name implies, is the generation of a gas, with low- to medium-energy contents, and a composition that can be used in subsequent synthetic processes. Gasification can be broadly divided into pyrolysis, partial oxidation, and reforming processes. Under very high pyrolytic temperatures the solid and

liquids phases will be suppressed, such that the gas is the main product. Partial oxidation uses less than the stoichiometric amounts of oxygen that would be needed to support combustion. This results in a partially oxidized product. Reforming in this context refers to gasification that is done in the presence of additional reactants, such as steam, steam-oxygen, or steam-air. The products of all of these processes are similar, with carbon monoxide and hydrogen being the main components of the gas. The energy content can range from $100\text{--}300\text{ Btu/SCF}$ (standard cubic foot) in processes that utilize direct contact of the wood with air (due to dilution), $300\text{--}700\text{ Btu/SCF}$ when oxygen is used, and $700\text{--}1000\text{ Btu/SCF}$ when conditions favor the formation of light hydrocarbons such as methane (which is responsible for a large proportion of the energy).

See also: **Medicinal, Food and Aromatic Plants:** Forest Biodiversity Prospecting; Medicinal and Aromatic Plants: Ethnobotany and Conservation Status; Medicinal Plants and Human Health. **Non-wood Products:** Resins, Latex and Palm Oil. **Sustainable Forest Management:** Definitions, Good Practices and Certification. **Wood Formation and Properties:** Chemical Properties of Wood. **Wood Use and Trade:** History and Overview of Wood Use.

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