

The effect of polarity of extractives on the durability of wood.

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ABSTRACT

Extractives are low molecular weight compounds and regarded as nonstructural wood constituents. These compounds are present in trees and can be extracted by organic solvents. Extractives consist of several classes of compounds that diversify the biological function of the tree. Fats are an energy source for the wood cells whereas terpenoids, resin acids, and phenolic substances protect the wood against microbial damage or insects. In this investigation, extractives from five softwoods and four hardwoods were separated into nonpolar and polar components. The softwoods used were southern yellow pine *Pinus glabra* (SYP), alaskan yellow cedar *Callitropsis nootkanensis* (AYC), eastern red cedar *Juniperus virginiana* (ERC), western juniper *Juniperus occidentalis* (WJ), and western red cedar *Thuja plicata* (WRC). The four hardwood species used were black locust *Robinia pseudoacacia* (BL), honey mesquite *Prosopis glandulosa* (HM), paulownia *Paulownia tomentosa* (PAW), and catalpa *Catalpa* (CAT). All these species except PAW and SYP are classified as durable/highly durable. The percentages of polar and nonpolar extractives for the softwoods are AYC 46 and 54, ERC 36 and 64, WJ 49 and 51, WRC 97 and 3, and, SYP 83 and 17. The percentages of polar and non-polar for hardwoods are BL 99 and 1, CAT 87 and 13, HM 99 and 1, and PAW 95 and 5. Literature ranks of durability of these woods in order from most to least were ERC > WJ > BL > HM > WRC > AYC > PAW < SYP < CAT. This ranking was derived based on weight loss from fungi and insect infection. Understanding of the role of extractives polarity on durability is important from the preservative and medicinal aspects. Analysis of the chemicals affecting the durability and mortality of wood will help in identifying chemicals for preservation of wood and those that have biological activity. Chemicals from nature will be environmentally friendly and cost effective.

KEYWORDS

Characterization, durability, fractionation, polarity, extractives

1. INTRODUCTION

The chemical composition of wood extractives is complex. These extractives are important in the growth and protection of the trees. Wood extractives are simple chemicals in wood that do not aid in structural integrity of the wood. These extractives are normally concentrated within the heartwood; however, their composition is known to vary not only from tree to tree but also change within a single tree.[1]

Kirker et. al., 2013 [1] studied unextracted and extractives-free woods using above-ground and below-ground testing. The study included below-ground field testing for 24 months on durable and non-durable woods. The above ground tests were soil block cultures and termite soil testing. The study showed that termites feeding on various extractive-free woods increased the rate of weight loss compared to the weight loss in unextracted woods. The order of durability of the various wood species was similar in both below and above ground results. Unextracted and extracted honey mesquite (HM) and black locust (BL) were exposed to eastern subterranean termites and the mortality rates of the termites were 96% and 70% respectively. The toxicity of the chemicals was killing the termites within a few days.

In this investigation, one of the attributes of extractives polarity will be investigated. Different organic solvents will affect the extractions of wood samples in different ways. The properties of the mixed organic solvents will increase or decrease the solubility of different wood extractives.

This study will characterize the chemical composition of extractives from nine durable and non-durable wood species. The extractives will be separated into non-polar and polar components. The non-polar component will be further fractionated into neutrals and acids. The chemical characteristics of various durable wood species will assist with discoveries of natural medicinal products and preservatives that will have commercial potential.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1. Wood Species

Wood species were obtained from various locations in North America. Naturally durable wood species were selected based on Kirker et al., 2013.[1] The general non-durable control was southern yellow pine *Pinus glabra* (SYP), alaskan yellow cedar *Callitropsis nootkanensis* (AYC), eastern red cedar *Juniperus virginiana* (ERC), western juniper *Juniperus occidentalis* (WJ), and western red cedar *Thuja plicata* (WRC). The four hardwood species used were black locust *Robinia pseudoacacia* (BL), honey mesquite *Prosopis glandulosa* (HM), paulownia *Paulownia tomentosa* (PAW), and catalpa *Catalpa* (CAT). All these species except PAW and SYP are classified as durable/highly durable.

2.2. Preparation of wood samples

The wood samples were cut and Wiley milled to 40 mesh. Each wood was processed separately, and the Wiley mill was cleaned between each wood milling to ensure no cross contamination. A soxhlet apparatus was used for extractions. Approximately 100 grams were extracted with 700 mL of 9:1 acetone:water for 10 hr (2 cycles per hour).

2.3. Separation of polar and non-polar extractives

The amount of dried acetone extractives were weighed in a pre-weighed 7 mL vial. 30 mL of Hexane and Chloroform (5:1) were used to separate the non-polar and polar components.[2] 5 mL were used per separation. For complete mixing of the extractives, each separation was sonicated and vortexed. The samples were allowed to settle for 10-15 min. The nonpolar fraction was decanted into a separate pre-weighed 7 mL vial. The remaining extractives in the original vial were the polar fraction. Nitrogen was used to evaporate solvent after each 5 mL separation. After the sixth separation both samples were dried completely under nitrogen and weighed. Two trials were performed on each wood species for consistency and variations in weigh.

2.4. Solid Phase Extraction of Neutrals and Acids

Nonpolar extractives were dissolved in 1 mL chloroform solvent. Amino propyl cartridges were pre-conditioned with 6 mL of hexane. Each sample was transferred into a pre-conditioned amino propyl cartridge and fractionated. The first fractionation (neutrals) were eluted with 8 mL hexane:diethyl ether (8:1), followed by the second fractionation (acids) with 8 mL diethyl ether:acetic acid (98:2). Samples were dried down in the hood and weighed.[2] All samples were duplicated.

3. RESULTS AND DISCUSSION

We know extractives play a role. However, this study is investigating the impact of polarity of extractives on durability. Table I was generated from Kirker et al., 2013.[1] The wood samples were extracted using 2:1 ethanol:toluene. The wood samples weight loss from the solvent extraction were between 3 and 13%. HM and WRC had the most solvent extraction weight loss 10 and 13% respectively. The soil block cultures and termite soil testing were evaluated using the extractive-free and unextracted wood samples. The percentages in the table showed insects preferred the extractive-free wood over the unextracted. WRC had the highest weight loss for the insect testing. This weight loss could be a result of the classes of extractives removed from the wood samples. The percentage weight loss of the wood blocks varied for each wood species for insect and wood decay testing. Each wood decay testing yielded different weight loss results for each wood species. The wood samples least durable in wood decay testing were CAT, PAW, and SYP. From this study we can conclude extracted wood species responded to insects and culture degradation testing.

Table I. Classification of the wood species above ground durability testing. [1]

Wood	Durable Against Rot	Durable Against Insects (DAI)	DAI Un-Extracted (Wt loss%)	DAI Extract. Free (Wt loss%)
AYC	Yes	Yes	--	36
BL	Yes	Yes	--	9
CAT	No	Yes	--	24
ERC	Yes	Yes	--	18
HM	Yes	Yes	--	--
WJ	Yes	Yes	--	15
PAW	No	Yes	--	44
SYP	No	No	2	31
WRC	Yes	No	5	51

--no weight loss

Figures 1 and 2 show the non-polar and polar mass percentages of the extractives removed from the nine wood species. The percentage of the extractives collected varied among each wood species. Chemicals usually found in the nonpolar component include fatty acids, resin acids, nonpolar phenols and oxidized resin acids, neutral terpenoids, phytosterols, waxes, triglycerides, and phytosterol esters.[2]

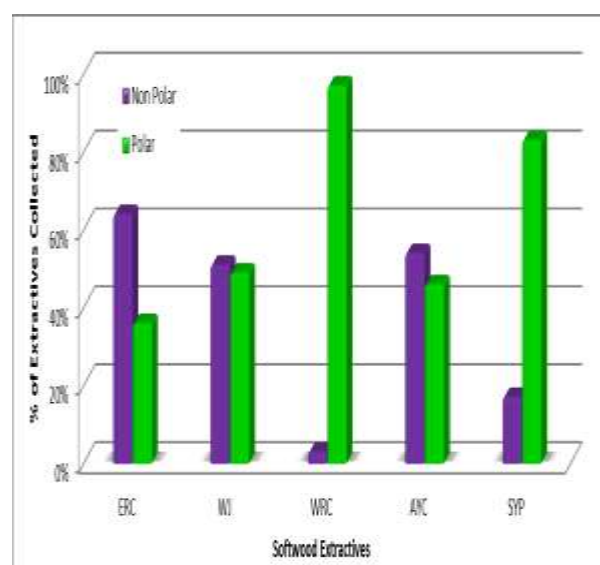


Figure 1. The mass percentage of non-polar and polar extractives collected from softwood lumber.

Literature states ERC is the most durable of the nine wood species. The order of durability is ERC>WJ>WRC>AYC>SYP for softwoods.[1] In softwoods, the percentage of nonpolar extractives decreases as the durability decreases and polar extractives increased as the durability decreased for the first three wood species (Fig 1). The AYC did not fit this trend. Highest weight loss for insects in softwoods was WRC (51%), AYC (36%), and SYP (31%) for extractive-free wood samples.[1] Each of these wood samples had over 40% polar extractives collected.

Percentages for non-polar compounds in hardwoods were below 20% for BL, HM, and CAT. All hardwood's polar component percentages were above 80%. BL and HM are among the top four durable wood species. The

insect testing results showed HM and BL mortality rate was 96 and 70%, respectively. The most durable wood species ERC rate was a minimum of 6.6%. After a few days of exposure to HM the insects were dead. The toxicity of the chemicals in the HM polar content could have played a major role in the mortality rate of the insects.

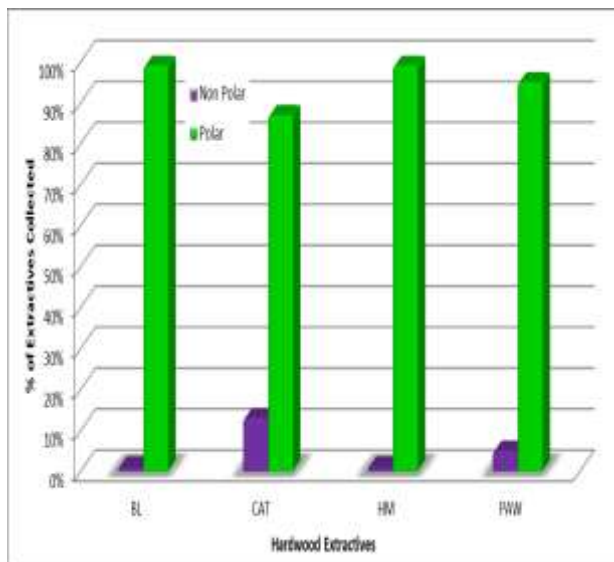


Figure 2. The mass percentage of nonpolar and polar extractives collected from hardwood lumber.

The polar chemicals include lignans, oxidized resin acids, phenols and low molecular weight carbohydrates.[2] The polar composition of BL and HM could have phenols with high toxicity causing the least weight loss. The non-polar components are rich with different classes of chemicals that can attribute to the durability of the softwood samples however, only 1% of the non-polar component was separated from the wood sample. Phenols are some of the chemicals that could play a role in the durability of BL and HM.

The composition of the polar component plays a major role in the durability of the BL and HM hardwoods. The extractives removed using 95% ethanol and toluene [1] did not lessen the durability of HM in the insect testing. The polarity of the solvent used did not affect the durability of the wood. The softwoods have both non-polar and polar extractives. The non-polar component acid fraction included fatty acids, resin acids, nonpolar phenols and oxidized resin acids. The neutral component included terpenoids, phytosterols, waxes, triglycerides, and phytosterol esters.[2] The resin acid, sterols and terpenoids are known for having anti-microbial activity. SYP has resin acids in both components. In the SYP, however, the concentration or the chemicals activity was not enough to hinder weight loss based on the results observed.

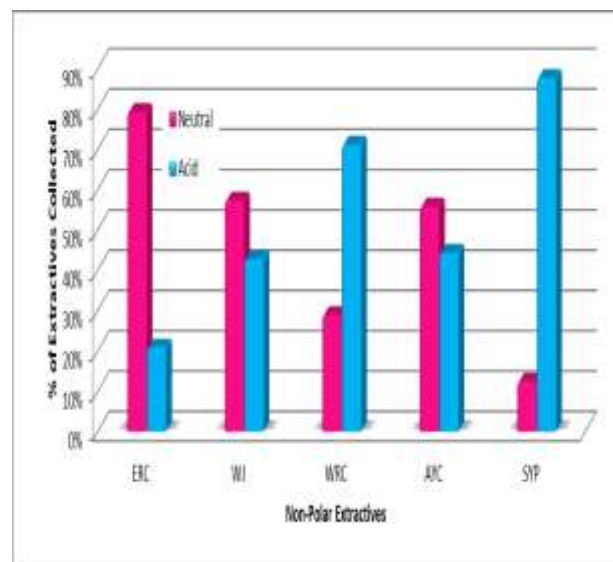


Figure 3. The mass percentage of softwood's non polar extractives fractionated into acid and neutral components.

Since the ratio of the nonpolar and polar components varied for the softwoods an additional fractionation into neutrals and acids was done to investigate the components further. The neutral components matched the trend seen earlier for the nonpolar component in Fig 1. For the softwoods, the neutral components in the nonpolar fraction decrease as the durability decreases. The nonpolar acids increase as the durability decrease. The hardwoods were not additionally fractionated because for most woods the nonpolar component was quite low. It is obvious that the polar component needs more investigation to determine which chemical has biological activity.

4. CONCLUSION

There are combinations of the chemicals in the non-polar and polar components that play a role in the durability in the nine wood species considered in this study. Chemicals known for reducing insect attack or biological activity on wood species are sterols, resin acids, phenols, as well as other specific wood-related chemicals. The Kirker *et al*, 2013 study on extractive-free and unextracted wood species demonstrated the importance of extractives on the durability by looking at weight loss from insect and wood decay testing. Polarity characteristic of extractives was investigated in this study. ERC, WJ, and WRC are the softwoods in the top six durable wood species. For ERC extractives, the mass percentage of the nonpolar component is 60%. The chemicals specific to this component with biological activity are sterols and resin acids. BL and HM are hardwoods in the top six durable wood species. The mass percentage of the polar component for these hardwoods was 99%. The chemicals identified in the polar component with biological activity are phenols.

The goal of future work is to identify specific chemicals in the non-polar and polar components used to reduce weight loss that could have biological activity.

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