CHINESE TALLOW TREE (*SAPIUM SEBIFERUM*) UTILIZATION: CHARACTERIZATION OF EXTRACTIVES AND CELL-WALL CHEMISTRY

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ABSTRACT

Wood, bark, and the wax-coated seeds from Chinese tallow tree (*Sapium sebiferum* (L.) Roxb. syn. *Triadica sebifera* (L.) Small), an invasive tree species in the southeastern United States, were subjected to extractions and degradative chemical analyses in an effort to better understand the mechanism(s) by which this tree species aggressively competes against native vegetation, and also to facilitate utilization efforts. Analysis of the wood extractives by FTIR spectroscopy showed functionalities analogous to those in hydrolyzable tannins, which appeared to be abundant in the bark; as expected, the seeds had a high wax/oil content (43.1%). Compared to other fast-growing hardwoods, the holocellulose content for the Chinese tallow tree wood was somewhat higher (83.3%). The alpha-cellulose (48.3%) and Klason lignin (20.3%) contents were found to be similar to those for most native North American hardwoods. Results suggest that Chinese tallow tree wood utilization along with commercial wood species should not present any significant processing problems related to the extractives or cell-wall chemistry.

Keywords: Cellulose, Chinese tallow tree, extractives, Klason lignin, utilization.

INTRODUCTION

Chinese tallow tree (*Sapium sebiferum* (L.) Roxb. syn. *Triadica sebifera* (L.) Small) is an invasive tree species in the southeastern United States with a range now extending along the Gulf States from Texas to North Carolina (Bruce et al. 1997). The common name is quite appropriate since the tree is native to China, where it has been cultivated as a valuable source of tal-

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low for more than 14 centuries (Bruce et al. 1997). The wax-coated seeds, which are persistent until winter (Miller 2003), resemble popcorn and thus another common name is the popcorn tree. The appearance of the seed, colorful fall leaves, rapid growth, and resistance to pests makes this species desirable as an ornamental that, despite its widespread encroachment on native ecosystems, is still sold and planted (Jubinsky 1993; Miller 2003). Allelopathy has been hypothesized as a mechanism by which the Chinese tallow tree can aggressively compete against native plants; however, some studies suggest that this is not the case (Keay et al. 2000; Conway et al. 2002). Recent findings also suggest that post-invasion adaptations may be involved that increase the tree's competitive ability over native plants (Siemann and Rogers 2001).

Interest in the Chinese tallow tree has historically focused on the recovery of the wax/oil for the manufacture of products such as soap and candles (Xu et al. 1991). More recently, various compounds, some with biological activity, have been isolated from the roots, bark, and leaves (Liu et al. 1988; Yang and Kinghorn 1985). Chinese tallow tree callus cultures have also afforded biologically active compounds (Neera et al. 1992). Aside from being a source of chemicals, this fast-growing tree has also been evaluated as a biomass resource. Field studies have shown that the Chinese tallow tree can produce four times as much biomass as fast-growing poplars grown in northern climates (Scheld and Cowles 1981). Given the invasive nature of the Chinese tallow tree, biomass utilization operations no longer favor cultivation but ultimately the control/eradication of the species throughout the southeastern United States.

Recently, research has demonstrated that the Chinese tallow tree can be used to make wood-based composites such as medium density fiberboard, particleboard, and flakeboards (Shupe et al. 2005). For medium density fiberboard, a lower level of performance for Chinese tallow tree wood fiber relative to other fiber resources was attributed to a higher relative proportion of fine fibers (Lee et al. 2004; Li et al. 2004). This problem was addressed using combinations with higher quality fiber resources such as bamboo (Li et al. 2004) and bagasse (Lee et al. 2004). For paulownia (*Paulownia tomentosa* (Thunb.) Sieb. & Zucc. ex Steud.), another very fast-growing hardwood, a high lignin content, and the high water solubility of the wood, were suggested to be advantageous to the physical and mechanical properties of particleboards (Kalaycioglu et al. 2005). A search of the literature did not provide information on the cell-wall chemistry of Chinese tallow tree wood. Therefore, as part of our continuing studies on Chinese tallow tree utilization, wood samples were subjected to degradative chemical analyses. Given the potential for whole tree harvesting, and the persistence of the wax-coated seeds, samples of bark and seed were also analyzed.

MATERIALS AND METHODS

Sample collection

Samples of wood, bark, and wax-coated seeds were taken from a Chinese tallow tree harvested in the month of October from a forest in East Baton Rouge Parish, Louisiana, USA; the seeds were still attached to the branches for easy collection. The bark was peeled from the wood at the time of harvest. After drying under ambient conditions, representative samples of the wood, bark, and seeds were each ground in a Wiley mill equipped with a 20-mesh screen. The mill was carefully cleaned before each sample to prevent cross-contamination.

Chemical analyses

Three aliquots of each sample were extracted (ASTM 1996a) in a Soxhlet apparatus with ethanol:toluene (7:3 by volume, 12 hours) and then ethanol (4 hours) to produce extractive-free tissues for Klason lignin (ASTM 1996b), holocellulose (ASTM 1971a), and alpha-cellulose (ASTM 1971b) determinations by standardized procedures. Sample weights were corrected for moisture contents determined by drying sample aliquots in an oven (103 ± 2ºC). Sample extracts

were concentrated by rotary evaporation, transferred to small glass vials, and then dried under a stream of N_2 to afford oils; residual solvent was removed by drying *in vacuo* using a vacuum desiccator. A separate sample of bark was also subjected to sequential extraction (20 hours each) with hexane, diethyl ether, 95% ethanol, and water. The organic-solvent extracts were processed as described above while the water extract was freeze-dried. Alkaline extraction (treatment) of extractive-free (i.e., ethanol-toluene and ethanol extracted) tissues (2 g) was carried out by treating with an aqueous solution of 1% NaOH (w/v, 100 mL) for 1 hour at 90°C (Labosky 1979). Samples were vacuum-filtered, washed with hot water (100 mL), 10% acetic acid in water (v/v, 50 mL), and then hot water until free of acid (TAPPI 1998). Yields of alkaline-extracted residue for the wood, bark, and seeds, each as a percent of the extractive-free tissue, were 80.7, 55.6, and 57.0%, respectively. Ash contents were determined using a muffle furnace set to 450°C. FTIR spectra were collected using a Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Smart Golden Gate MKII Single Reflection ATR accessory. Extracts were analyzed directly by applying a small amount of dry extract directly on the diamond crystal.

RESULTS AND DISCUSSION

The extractives and cell-wall chemistry of the Chinese tallow tree are of interest from two perspectives. First, the mechanisms by which this tree species aggressively competes against native vegetation are not well understood and/or conflicting. Secondly, a basic understanding of this biomass resource is necessary for facilitating any utilization effort. It was surprising to find that despite the existence of extensive compilations of wood chemistry data (Pettersen 1984), values for this species were not available. Standard methods of analysis were applied here to permit comparisons to reported data. One exception was that the alkaline extractions were carried out on the extractive-free tissues instead of directly. Our goal was to remove both the readily accessible extractives and the intractable materials (e.g., cross-linked tannins, suberin) known to cause an overestimation of the lignin contents determined for bark tissues (Laks 1991).

The ethanol-toluene extraction of the wood samples (Table 1) afforded an average extractives content of 4.8%, which is between the 3% for a native fast-growing pioneer tree species, poplar (*Populus tremuloides* Michx.), and the 8% reported for another invasive species, paulownia, that were obtained by ethanol-benzene extraction (Pettersen 1984). Subsequent extractions of the wood samples with ethanol removed only small amounts of material. Analysis of both wood extracts by FTIR spectroscopy afforded similar spectra; however, that for the ethanol extract showed somewhat less signal resolution. Carbonyl (1720 cm^{-1}), aromatic C=C stretch (1600 cm^{-1}), and aromatic C-C vibration (1500, 1450 cm^{-1}) signals (Fig. 1, Spectrum A) observed for the wood extracts were consistent with the functionalities in hydrolyzable tannins. Determination of the level of extractives was of particular interest since phenolic extractives (e.g., hydrolyzable tannins) have been shown to interfere with the cure of phenolic resin systems used in wood composite manufacture (Plomley et al. 1976; Tohmura 1998).

TABLE 1. *Chemical constituents of Chinese tallow tree wood, bark, and seeds.*

	Tree component		
	Wood (%)	Bark (%)	Seeds (%)
Extractives:			
Ethanol:toluene (7:3)[a]	4.8 ± 0.3	24.2 ± 2.2	43.1 ± 3.1
Ethanol[a]	0.3 ± 0.1	0.5 ± 0.1	2.0 ± 0.5
Total[a]	5.1 ± 0.3	24.7 ± 2.2	45.1 ± 2.7
Ash[a]	0.7 ± 0.0	6.5 ± 0.5	nd
Holocellulose[b]	83.3 ± 0.7	67.1 ± 3.4	38.6 ± 3.6
Alpha-cellulose[b]	48.3 ± 0.1	40.8 ± 0.1	18.9 ± 0.5
Klason Lignin:			
Extractive-free tissue[b]	20.3 ± 0.1	33.6 ± 1.8	53.5 ± 2.8
Organic solvent and 1% NaOH extracted tissue[b]	16.2 ± 0.3	16.7 ± 0.2	31.6 ± 0.2

[a] Percents based on oven-dry weight of the unextracted tissues, nd = not determined.
[b] Percents based on oven-dry weight of the extractive-free (i.e., ethanol-toluene and ethanol extracted) tissues.

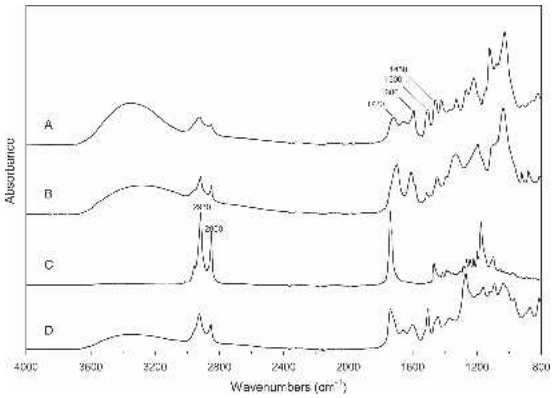

FIG. 1. Infrared spectra of ethanol:toluene (A, wood; B, bark; C, seeds) and ethanol (D, seeds) extracts from Chinese tallow tree samples.

As expected, ethanol-toluene extraction of the bark afforded a much higher average extractives content (24.2%) than that for the wood. Extraction with ethanol gave an extract that had a similar composition as evidenced by an FTIR spectrum with essentially the same fingerprint. Signals for the bark extracts (Fig. 1, Spectrum B) were consistent with those expected for hydrolyzable tannins. Finally, the ethanol-toluene extraction of the seeds afforded a high amount of wax/oil (43.1%) similar to that reported in the literature (Xu et al. 1991). The presence of aromatic signals for the ethanol extracts from the seeds (Fig. 1, Spectrum D) suggested the possibility that the seeds may also contain compounds analogous to the hydrolyzable tannins that appeared to be present in the bark.

In the case of the Chinese tallow tree seeds, the very sharp aliphatic C-H signals at 2920 and 2850 cm^{-1} (Fig. 1, Spectrum C) showed the presence of waxy materials. Similar signals, although of significantly lower intensity, were also present for the bark. A sample of bark was subjected to sequential extraction with solvents of increasing polarity to provide an indication of the distribution of the different extractives types. Extraction of the bark in this manner gave hexane (2.6%), ether (0.5%), 95% ethanol (14.8%), and water (5.8%) soluble extractives with the average total amount being a value (23.7%) that was nearly the same as that obtained by ethanol-toluene extraction. Analysis of these extracts by FTIR spectroscopy (spectra not shown) verified the presence of mostly waxy materials in the hexane and diethyl ether bark extracts. The spectrum for the 95% ethanol extract was similar to that for the spectrum for ethanol-toluene extract from the bark.

The extractive-free tissues obtained were subsequently subjected to degradative chemical analyses to determine average values for holocellulose, alpha-cellulose, and Klason lignin. Compared to the other above-mentioned fast-growing tree species, the average holocellulose content was somewhat higher (83.3%). The average alpha-cellulose content (48.3%) was essentially the same as those reported for paulownia (Kalaycioglu et al. 2005) and poplar (Petterson 1984) woods. Coinciding with these values for the cell-wall carbohydrates was an average Klason lignin content of 20.3%. At this juncture, it should be recalled that the lignin contents of hardwoods tend to be lower than those for many softwoods. While it is beyond the scope of this study, it is worth mentioning that along with the evolution of vascular plants, there appear to be adaptations of both the level of lignification and the structure of the macromolecule as evidence by different ratios of the basic building units, the monolignols (Lewis et al. 1999). Further studies are needed to better understand the structure of the Chinese tallow tree lignin to identify any relationships to the ability of this species to aggressively compete against native plant species. From the perspective of utilization, the possible relationships between wood composite performance and the cell-wall chemistry of the wood are not completely understood. Given that the analysis of Chinese tallow tree wood generally gave data that were similar to those reported for fast-growing commercial species, it would appear that we cannot exclude the use of Chinese tallow tree wood along with commercially harvested wood species on the basis of its extractive or cell-wall chemistry.

The lignin contents of Chinese tallow tree leaf litter have been reported in a study assessing impacts on soil quality (Cameron and Spencer 1989). A literature search did not yield lignin

content values for Chinese tallow tree bark or seeds. The results from our chemical analyses showed values for holocellulose and alpha-cellulose for the bark were intermediate (67.1%) to those determined for the wood and the seeds. As expected, the average Klason lignin content of the bark (33.6%) was high when determined on the extractive-free tissue. Given that intractable bark constituents (e.g., cross-linked tannins, suberin) can contribute to the value for lignin content, alkaline extraction was used to afford a residue from which more representative lignin contents could be determined. The data shown here suggest that the Klason lignin contents for the alkaline-extracted bark and wood were essentially the same on the basis of the extractive-free tissues. Given that ash can carry over to the Klason lignin collected, the high average ash content for the bark (6.5 ± 0.5%), relative to that for the wood (0.7 ± 0.0%), could lead to the conclusion that the true value for the lignin content of the bark is lower than the value shown. For the seeds, alkaline extraction also resulted in a significantly lower average Klason lignin content relative to that for the extractive-free tissue. Given the high amounts of material removed from the bark and seed samples by the organic-solvent and alkaline extractions, high amounts of bark and seed in a Chinese tallow tree wood supply would likely result in a noticeable increase in the chemical requirement for operations such as chemical (e.g., kraft) pulping; problems in composite manufacture may also be significant.

CONCLUSIONS

Analysis of our Chinese tallow tree wood samples gave data that were generally similar to those reported for fast-growing commercial wood species. Therefore, it would appear that we cannot exclude the industrial use of Chinese tallow tree wood along with commercially harvested wood species on the basis of its extractive or cell-wall chemistry. Analysis of the seed extracts by FTIR spectroscopy suggested that along with an abundance of wax/oil, the seeds may also provide a source of biologically active compounds analogous to the hydrolyzable tannins that appear to be abundant in the bark. Klason lignin determinations, carried out before and after alkaline extraction, along with the results from ash determinations, suggest that the Klason lignin content of the bark is lower than that for the wood.

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