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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 20(4), 415–439 (2000)

KNOT, HEARTWOOD, AND SAPWOOD EXTRACTIVES RELATED TO VOCs FROM DRYING SOUTHERN PINE LUMBER

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ABSTRACT

The presence of knots or heartwood influences the amount and composition of volatile organic compound (VOC) emissions associated with drying of southern pine lumber. Experimental kiln charges of lumber containing 0 to 5% of knot volume gave VOC emissions ranging from 2.86 to 4.25 lb of carbon/dry ton of wood. Studies of emissions from sapwood and knots showed that knots contain about ten times the amount of volatile terpenes found in sapwood. Consequently half of the total volatile emissions would come from 5% of knot volume in sapwood. However, correlation coefficients of knot frequency or volume with VOC emissions obtained from experimental kiln studies were only 0.57 and 0.51, respectively. Southern pine heartwood contains about five times the amount of volatile terpenes found in sapwood and more of the volatile

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compounds present in heartwood are emitted than from knots. Therefore, small variations in the amount of heartwood result in large changes in VOC emissions in drying southern pine lumber.

INTRODUCTION

Virtually all of the published literature available on the chemistry of southern pine terpenes has been directed to understanding the chemical properties of clear wood,[1] oleoresin exudates (naval stores) obtained from gum rosin,[2,3] old stumps,[4] or tall oil.[5] Although plant terpenes have been studied intensively,[6] little attention has been directed to the differences in the chemistry of knots, heartwood and sapwood.[7,8] This deficiency is especially surprising relative to the Southern pines because knots and "red heart" are well known to contain such high levels of extractives that they are often used as "lighter wood" to build fires. In exploratory experiments to compare the amounts of extractives in clear wood and knots from freshly felled timber in Louisiana, knots contained approximately 30 times the amounts of dichoromethane-soluble extractives as were extracted from the adjacent clear sapwood.[9]

Because of continually increasing concerns about volatile organic compound emissions (VOC) associated with the drying of wood products,[10-12] efforts to understand sources and reduce VOC emissions from drying wood will continue. A useful review of air quality concerns related to lumber and wood products manufacture is provided in EPA's Sector Notebook Profile of the Lumber and Wood Products Industry.[13] Even though the U.S. Court of Appeals has struck down the new 0.8 ppm total VOC emission and 2.5 μm diameter particulate matter standards proposed in the Clean Air Act,[14] efforts to understand the sources and mitigate VOC emissions associated with drying wood must continue. Both volatile terpenes and higher molecular weight organic aerosols derived from the wood itself are of concern, not because of their toxicity, but because of their influence on formation of ozone and blue-haze due to small particulates. Therefore, the questions: a) what compounds are found in knot,

heartwood, and sapwood extractives and b) how do they influence the amount and composition of VOCs emitted in the drying of southern pine lumber came to fore.

Preliminary work on the significance of knot extractives led to comparisons of both sapwood and heartwood as sources of volatile terpenes in drying southern pine lumber. Published research directed to drying of southern pine[15-17] and Douglas-fir[18] demonstrates wide variations in amounts of VOC emissions related to the wood species and the schedule used to dry structural lumber. It was postulated that the wide variations in VOC emissions observed in drying lumber could be due to variations in the amounts of knots and/or heartwood in the lumber.

EXPERIMENTAL

Work on this project was done at two laboratories, the Southern Research Station's Laboratory (SRSL) at Pineville, LA and the Mississippi Forest Products Laboratory (MFPL) at Mississippi State University. Different procedures were sometimes used because of the type and availability of equipment at the two laboratories. This dual effort sometimes resulted in duplication, but that proved to be an advantage as results obtained at the two laboratories were generally consistent and added support to the conclusions reached in this study. Although the primary focus of this work was on drying of lumber, higher temperature conditions were examined to give some insight into what contributions knots or varying amounts of heartwood might have to VOCs associated with the drying of southern pine veneer.[19]

Extraction and Methylation of Extracts from Knots and Clear Wood.

Freshly sawn green loblolly pine lumber was collected from a portable sawmill in Louisiana. Knot and adjacent clear wood tissues were removed with a band saw and samples were either extracted with dichloromethane immediately or wrapped in aluminum foil and zip-lock bags and stored frozen until use. The frozen knot or wood tissues were ground with a wood rasp into a receiver containing dichloromethane. The extract was recovered by filtration through

glass wool and concentrated on a rotary evaporator taking care not to subject the product to prolonged drying. The sample was then methylated with excess ethereal diazomethane and analyzed by gas chromatography-mass spectrometry (GC-MS).

For preliminary analyses of the amount and composition of dichloromethane soluble materials in samples collected in Mississippi, one knot tissue plug and two clear wood plugs were ground in a Wiley mill. The ground tissue (10 to 20 g) was combined with 20 g of sodium sulfate in a cellulose extraction thimble. The sample was extracted in a Soxhlet with 225 mL of dichloromethane and 5 mL of a solution of 1,4-dichlorobenzene (1 mg/mL) in dichloromethane for 16 h. The samples were cooled and 1 mL of diphenylmethane (1 mg/mL) in dichloromethane was added as an internal standard prior to concentration to 10 mL. These extracts were examined by a GC.

Poor correlation (R^2 of 0.57 - 0.51) between the number of knots or knot volume with VOC emissions measured in drying experiments performed in an experimental kiln (see below) prompted further study to examine the effect of heartwood on VOC emissions. A 45-year-old loblolly pine tree was felled, the limbs removed, and the bole of the tree cut into four 10-ft lengths and transported to the MFPL. Samples of knots, heartwood, and sapwood were removed from each section and the sapwood or heartwood surrounding knot samples was removed with a band saw and a wire brush. The undried samples were ground in a Wiley mill using a 6 mm screen and stored in zip-lock bags at -4°C.

Cellulose extraction thimbles were weighed and filled with approximately 30 g of ground sapwood or heartwood. For knot tissue, only 10 g of sample were extracted. The tissues were extracted overnight in a Soxhlet with dichloromethane. The sample dry weight was determined by reweighing the ovendry tissue and thimble. After extraction a 500 mL flat bottom flask fitted with a Snyder column was used to concentrate the dichloromethane solution to 100 mL. Ten mL of 1 mg/mL diphenylmethane in dichloromethane was added as an internal standard. A 1 mL aliquot of the sample extract was reacted with diazomethane in diethyl ether prior to analysis by GC. Extraction and recovery

efficiency was evaluated by adding known amounts of the compounds: α-pinene, camphene, β-pinene, limonene, borneol, fenchyl alcohol, and 4-allylanisole to extractive-free wood samples that were processed as described above. Recovery values for these compounds at two different concentrations ranged from 75 to 110% and averaged 93%.

Gas Chromatography-Mass Spectrometry Analysis

Analyses at the SRSL were carried out on a Finnigan MAT GCQ system. MS spectra were compared with National Institute of Science and Technology (NIST), Georgia Pacific, Terpene, and our own library. GC analyses were on a 30 m x 0.25 mm column with a DB-5 film at a thickness of 0.25 μm. The GC program was 1 min at 45°C and then a linear 15°C/min ramp in temperature from 45 to 280°C, after which the column temperature was held at 280°C for 10 min.

Analyses at the MFPL were carried out on a Kratos MS-80 RFA spectrometer and spectra were processed using Kratos MACH-3 software. Spectra were compared to the Wiley NBS Mass Spectral Database. The GC analyses were first made using a 30-m x 0.32-mm id column with a DB-625 film at a thickness of 1.0 μm. The oven temperature program was 60°C for 2 min, a linear ramp of 6°C/min to 280°C and then 20 min at 280°C. Other separations were made on a 30-m x 0.32-mm column with a DB-5 film at a thickness of 1 μm. The oven temperature program was 2 min at 60°C and a linear 6°C/min ramp to 250°C. Most terpenes and fatty acids were identified by comparison of the retention time and MS fragmentation with those of authentic compounds (labeled RT).

Column and Thin-Layer Chromatography

Some of the aromatic compounds (4-allylanisole, dimethyl pinosylvin, methyl pinosylvin, and methyl pinocembrin) were isolated by making first separations by flash column chromatography on silica using increasingly polar mixtures of hexane/ethyl acetate. Fractions from the flash column were

monitored with thin layer chromatography on silica gel plates developed using hexane/ethyl acetate at various proportions and using ultraviolet (UV) absorbance and color reactions with anisaldehyde as indicators. These fractions were purified further by column chromatography or preparative thin layer chromatography (TLC) plates and their structures verified by nuclear magnetic resonance (NMR). NMR experiments were carried out on a Bruker AC-300 system. ^{1}H, COSY, ^{13}C, DEPT, and H-C HETCOR experiments were used to verify the identity of 4-allylanisole, methyl pinosylvin, dimethyl pinosylvin, and methyl pinocembrin. ^{1}H and ^{13}C NMR spectra of the major monoterpenes isolated were compared with spectra obtained from authentic compounds obtained from Aldrich Chemical Co. Inc.

Volatile Organic Compounds Emitted from Clear Wood and Knot Tissues

Experiments to compare the amounts of VOC obtained from heating wood and knot materials were done at both the Southern Research Station and at Mississippi State University. At the Southern Research Station, blocks of clear wood or knot tissue (about 1 x 1 x 10 cm each and totaling between 15 and 20 g) were placed in a glass tube. The tube was wrapped with heating tape connected to a voltage regulator to provide temperatures of 100, 120, and 155°C. The samples were heated for 4 h with air flowing through the tube at a flow rate of approximately 250 mL/min. The outlet of the heating tube was connected to a cold trap kept at -40°C. A condensate that formed between the end of the heating tube and the cold trap was dissolved with dichloromethane and added to the contents of the cold trap. The water and dichloromethane-soluble distillate in the combined sample were separated into water- and dichloromethane-soluble fractions using two separations with dichloromethane in a separatory funnel. The dichloromethane-soluble fraction was dried over sodium sulfate, made to constant volume and injected directly into the GC or was dried on a rotary evaporator and weighed prior to making them to constant volume and injecting those samples into the GC. In most samples, diphenylmethane was added as an internal standard.

Similar experiments were conducted at Mississippi State University by heating five samples of knots. Strips of knot tissue ranging in size from 2 to 12 mm in thickness were cut with a band saw from green 2 in x 6 in lumber obtained from a sawmill in Mississippi. The knot tissue was placed in a 500-mL resin kettle that was fitted with a cold trap submerged in an ice bath. The resin kettle was heated at 140°C for 19 h. The weight of knot tissue before and after heating as well as the weight of volatile oil collected in the trap was recorded. For GC-MS 0.1 to 0.15 g of the distillate oil was dissolved in 20 mL of dichloromethane and a 2 μl sample was injected onto a DB-5 capillary column and analyzed as described above.

Additional experiments were made to compare the amounts of volatiles obtained from knots, heartwood, and sapwood. Samples of each tissue type were cut into cubical blocks approximately 2.5 cm square and heated in a 500-mL resin kettle. The top of the container was fitted with a Teflon line that was connected to two cold finger traps in series, one at 0°C and the other at about –40°C. The resin kettle was heated in a Varian GC oven at 115°C for 20 h. The contents of the 0°C trap were transferred to a screw cap test tube at the end of 0-4, 4-8, and 8-20 h. Visible amounts of condensate were not observed in the second -40°C trap. In experiments with knots and heartwood and the 0-4 h sapwood the oil and water layer were separated using a pipette. The weight of the oil was determined. A 20-μL aliquot of the oil layer was diluted to 10 mL in dichloromethane and diphenylmethane was added as an internal standard. After transferring 1-mL aliquots to auto-sampler vials, each sample was methylated overnight with approximately 20 drops of diazomethane in ether. The total distillate was extracted with dichloromethane in samples obtained from the 4-8 and 8-20 h sapwood samples. Gas chromatography was performed on a Varian 3600 GC fitted with a 30-meter (0.32 mm id and 1 μm film) J & W BD-5.625 column with injector and detector temperatures at 280°C. The oven temperature was maintained at 60°C for 2 min and then increased to 280°C at 6°C/min.

VOCs from Lumber Dried in an Experimental Kiln

Lumber (2 in x 6 in x 8 ft) from a sawmill in Mississippi was sawn to 23

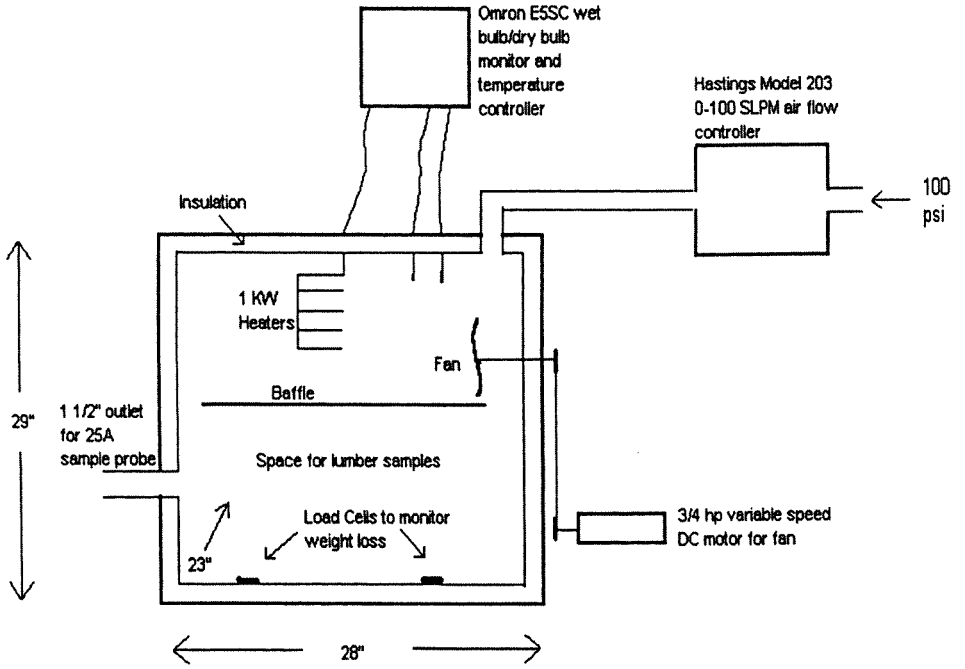

FIGURE 1. Design of The Experimental Kiln Used to Measure VOC Emissions in Drying Lumber at Mississippi State University.

in (58 cm) length and samples were sorted to give nine kiln charges (15 boards per charge) with a range of knot content (i.e., 0, 2, 4, 6, 8, 9, 11, 13, and 15 knots per kiln charge). The lumber was dried in an experimental kiln (Fig. 1) that was heated with four 1-kW electrical heaters controlled by a Dwyer temperature controller. The target dry-bulb temperature was 240°F (115°C). The air flow rate in the kiln was controlled at 2.00 standard cubic feet per minute (scfpm) with a Hastings Model 203 flow controller that gave a wet-bulb temperature in the range from 150 to 180°F (65 to 82°C). With a drying time of 18 h, the final moisture content of the lumber ranged from 7 to 10%.

A Thermo Environmental Model 51 total hydrocarbon analyzer was used to determine the concentration of VOCs in the kiln exhaust. Zero-grade hydrogen

and air were used for the detector. Certified calibration standards of propane in air were used to calibrate the instrument in the range of 0 to 1,200 ppm. The average concentration of VOC emissions was determined for each complete drying cycle. The weight of VOC emission was calculated as pounds of carbon/dry ton of lumber:

$$\text{Wt (g)} = \frac{3 \times \text{TWA ppmv} \times 1 \text{ atm} \times 12.011 \text{ g/mole} \times (\text{vol of air} + \text{vol of water})}{82.050 \text{ cc}\cdot\text{atm K}^{-1} \text{ mole}^{-1} \times 293°\text{K}}$$

$$\text{VOC (lb/dry ton)} = \frac{\text{Wt (g)} \times 2{,}000 \text{ lbs/ton}}{\text{Wt of lumber (lbs)} \times 453.6 \text{ g/lb}}$$

For this calculation, 3 equals the number of carbons per propane molecule; TWA ppmv equals the time weighed average of VOCs as determined with the total hydrocarbon analyzer; Vol of air and Vol of water vapor are Volumes of vapor in m^3.

RESULTS AND DISCUSSION

Amounts and Composition of Dichloromethane-Soluble Extractives in Knots, Heartwood, and Sapwood.

In the first exploratory studies on lumber from a Louisiana sawmill, crude dichloromethane extract yields from knots ranged from 24 to 42% and averaged 31.5% of ovendry knot weight. Similar extractions from clear sapwood ranged from 0.6 to 1.1% and averaged 0.8% of wood dry weight. The high yields of extracts found from the knots examined in this trial prompted us to explore the amount and composition of dichloromethane-soluble extractives isolated from knots and sapwood obtained from green loblolly pine lumber collected from a sawmill in Mississippi. The composition of these extracts was also compared to a sample of loblolly pine oleoresin isolated as an exudate from a green tree.[4] A diphenylmethane internal standard was added to permit a comparison of the relative proportions of compounds in these extracts. The extracts were methylated and analyzed by GC-MS. The results of the Mississippi study showed that the complexity of both the monoterpenes and resin acids were higher in knot extracts than in the sapwood or oleoresin (Table 1).

TABLE 1
Relative GC-MS Peak Intensity of Compounds Found in Knot, Sapwood, and Oleoresin Extracts

Compound	Identification	Knots (1)[a]	Sapwood[a]	Oleoresin[a]
Tricyclene	Lib	0.02		
α-Pinene	RT	4.9	0.15	2.8
Camphene	RT	0.4	0.1	
β-Pinene	RT	3.0	0.22	1.3
Myrcene	RT	0.6		
Limonene	RT	1.3		0.37
α-Terpinolene	RT	0.4		
Fenchyl alcohol	RT	0.5		
Borneol	RT	0.5		
α-Terpineol	RT	-[b]		
4-Allylanisole	NMR	2.8[b]		0.28
Epijuvabione	Lib	1.9		
Methyl oleate	RT	0.31		
Methyl sterate	RT	0.79		
Dimethyl pinosylvin	NMR	4.2		
Methyl pimarate	RT	1.3	0.12	0.47
Methyl isopimarate	Lib	-		
Methyl sandaracopimarate	RT			
Methyl palustrate	RT	-c		
Methyl pinosylvin	NMR	-c		
Methyl levopimarate	Lib	2.7[d]	0.49	1.5
Methyl dehydroabietate	RT	3.2	0.18	0.60
Methyl abieatate	RT	2.6	0.36	0.60
Methyl pinocembrin	NMR			
Methyl neoabietate	RT	1.6	0.60	0.60

[a] Analysis of samples collected in Mississippi and analyzed by GC-MS at Mississippi State using diphenylmethane as an internal standard, GC separation on a DB-625 column. Addition of the internal standard allows comparison of relative peak intensities as an estimate of relative amount of each compound in the same amount of tissue or extract. Acids were identified as their methyl esters.

[b] α-terpineol and 4-allylanisole are not well resolved.

[c] On the DB-625 column these three compounds are not well resolved.

[d] Methyl pinosylvin was isolated and proven by NMR. Not well resolved from methyl levopimarate on a DB-5 column.

These preliminary experiments have shown that knots contain far more total volatile material than sapwood. Both the amounts and composition of extractives in knots are highly variable. The high variability between knot samples proved to be one of the major challenges of this work. Most important from the standpoint of potential VOC emissions associated with drying of southern pine lumber or veneer is the fact that both the amounts and complexity of the composition of volatile monoterpenes and aromatics present in knots are indeed orders of magnitude higher than in sapwood. Although resin acids dominate knot extracts, significant proportions of monoterpenes are found. The potential for knots to contribute importantly to VOC emissions in manufacture of either southern pine lumber or veneer certainly is present. Potentially, a substantial amount of the VOC emissions associated with drying southern pine lumber or veneer could come from knots if knot tissue made up only 2-5% of the volume of the material being dried.

Amounts and Composition of VOCs Obtained from Drying Knots and Adjacent Clear Sapwood.

The weight loss seen in heating small "sticks" of green knot and adjacent green sapwood, as expected, showed that far less total weight is lost from heating the knot tissues in air flowing through a heating tube (Table 2). The sapwood samples lost close to half (39 to 49%) of their weight as would be expected from drying green wood of a moisture content of close to 90% on a dry weight basis. In contrast to drying wood, similarly sized "sticks" of knots lost only 10 to 18% of their green weight under the same drying conditions. Because of their high density and extractive content, knots hold far less water than wood. However, water is by far the major volatile component removed from either wood or knots.

Attempts to measure the amounts of dichloromethane-soluble materials gravimetrically were hindered by the fact that we could not take the sample to a constant weight because of loss of volatile monoterpenes. Therefore, the gravimetric results greatly over-estimated the actual yield of products. To interpret the chromatograms obtained from the Finnigan GCQ system, we built

TABLE 2.
Total Weight Loss and Relative Amounts of Volatile and High Boiling Point Compounds Emitted from Knots and Clear Sapwood After Heating for 4 h at 100, 120, and 155°C.

Tissue	Sapwood			Knots		
Drying Temperature (°C)	100	120	155	100	120	155
Total Weight Loss (% of tissue dry wt.)	39.3	47.1	49.2	10.3	16.4	17.7
Dichloromethane-Soluble Distillate GC-MS Identifiable Volatiles (mg/g)	0.60	0.55	0.92	2.6	4.6	15.0

calibration curves for α-pinene, β-pinene, 4-allylanisole, methyl palmitate, methyl oleate, methyl pimarate, methyl isopimarate, and methyl dehydroabietate to obtain response factors in comparison with diphenylmethane. Yields were estimated yields from the major products observed in the chromatograms using those calibration curves as the total GC-MS identifiable volatiles.

The amounts of dichloromethane-soluble materials recovered from heating the sapwood ranged from 0.05 to 0.09% of the sapwood weight (Table 2). In earlier work, Punsuvon[16] found volatile oil yields ranging from 0.021 to 0.064% of the dry weight of loblolly pine sapwood. The amounts of distillate obtained from the knot tissues are, as was expected, much higher than obtained from sapwood. Even though there are far higher amounts of potentially volatile compounds in the knots, the amounts of distillate obtained from knots were only about 5 to 10 times higher than those obtained from sapwood unless the knots were heated to high temperatures (155°C).

A surprising result was the comparatively low proportion of volatile material in the knot distillate (Table 2) as compared to the amount present in the unheated knot (Table 1). The effect of high temperature seen in heating knots at 155°C was supported by work at Mississippi State where strips of knot tissue ranging in thickness of 2 to 12 mm were heated at 140°C for 19 h to once more

emphasize the high variability in properties of southern pine knots, the moisture content of five knot samples ranged from 19 to 41%. The amount of volatile oil collected ranged from 2.73 to 4.68% of the dry knot weight.

The composition of the distillate was highly dependent on whether the sample was sapwood or knot tissue. Figure 2 shows a comparison of the chromatograms of methylated dichloromethane-soluble materials obtained from heating sapwood and knots at 120°C for 4 h. The comparatively high levels of diterpene resin acids found in the distillate from knot tissues was surprising given the fact that their vapor pressure at 120°C is low. However, in these experiments we also collected the dichloromethane-soluble condensate in the transfer line between the heating tube and the cold trap. The fatty acids (methyl palmitate and methyl oleate) and the resin acids (methyl pimarate, methyl isopimarate and methyl dehydroabietate) were found as major components of the methylated distillate in the sapwood samples heated at 120°C. Comparatively high proportions of resin acids were also found in the distillates obtained from knots heated at 120°C. They were probably present as the major portions of the condensate found in the transfer line that was added to the materials in the cold trap in these experiments. In experiments at Mississippi State University where there was no air flowing through the heated samples, resin acids were not found or were only found in trace amounts.

Heating temperature was especially important to the amounts of high molecular weight materials recovered in the transfer line. As expected, the monoterpenes α-pinene and β-pinene together with 4-allylanisole, made up the majority of the materials identified in the 100°C distillate. Significant amounts of methyl pimarate, methyl isopimarate, and methyl dehydroabietate were found in the 120°C (Fig. 2) and especially in the 155°C distillates.

Table 3 provides a summary of the major components found in GC-MS analyses of the methylated distillates obtained from heating sapwood and knots at 100, 120, and 155°C for 4 h. The compounds listed here accounted for approximately 80% of the weight of compounds that were identified. These results must be interpreted with caution because of the high degree of variability

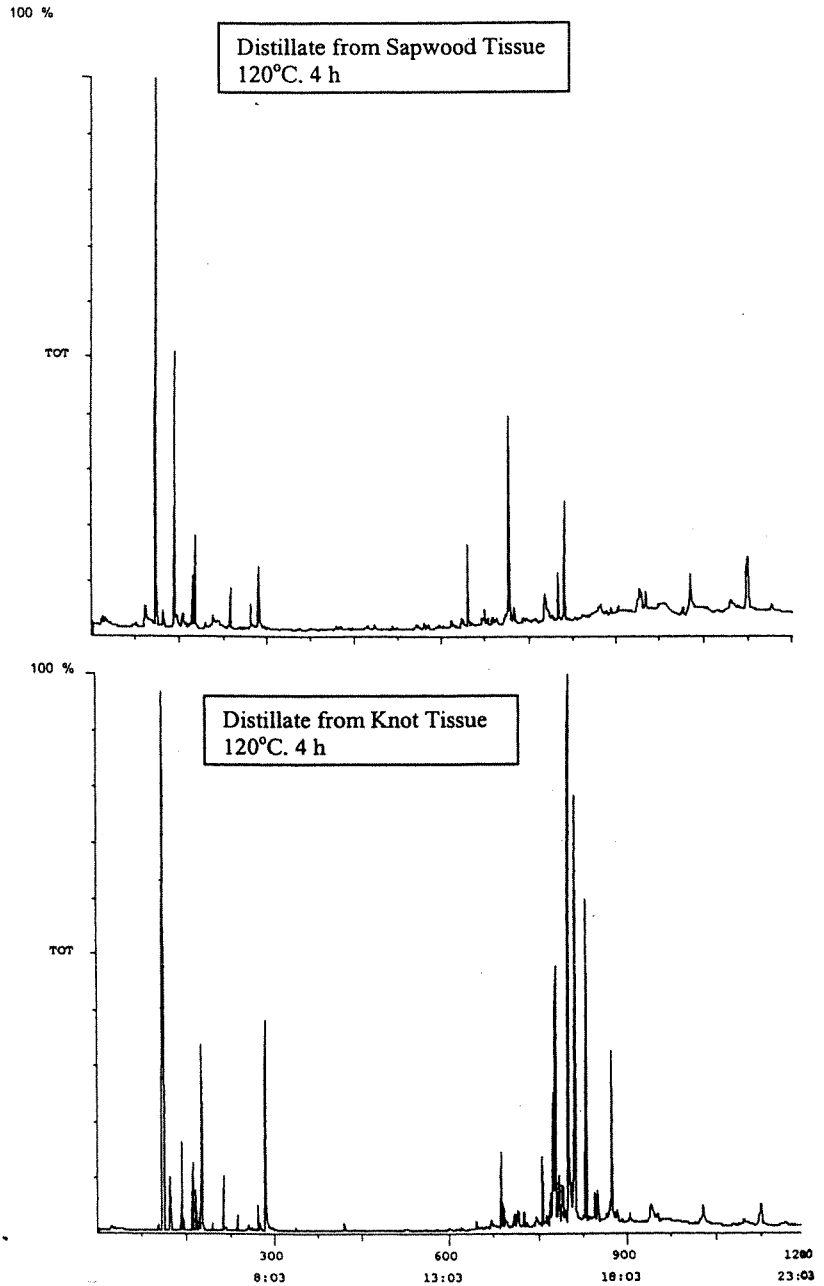

FIGURE 2. Composition of Distillates from Sapwood and Knots Heated at 120°C for 4 h. (As mentioned above, peak areas are not representative of the amount of compound present).

TABLE 3.
Amounts of Major Compounds in the Methylated Distillate Obtained From Heating Sapwood and Knots

Tissue	Sapwood			Knots		
Temperature (°C)	100	120	155	100	120	155
Compound			(μg/g of Tissue)			
α-Pinene	225	198	17	1,313	1,222	7,740
β-Pinene	178	133	14	499	371	1,810
4-Allylanisole	34	22	14	188	344	1,095
Methyl Palmitate	10	15	90	<1	<1	<1
Methyl Oleate	20	41	406	<1	<1	<1
Methyl Pimarate	<1	5	22	10	477	261
Methyl Isopimarate	2	6	34	24	647	578
Methyl Dehydroabietate	7	18	145	23	654	528
			(mg/g of Tissue)			
Total	0.48	0.44	0.74	2.1	3.7	12.0

in amounts and composition of distillates, especially among those from the knot samples. It is important to note the reduction in amounts of volatile terpenes obtained from sapwood heated at 155°C. Thermal/oxidative rearrangements of monoterpenes at high temperatures may be the cause of this reduction.[20]

A consolidated summary of all the compounds identified in the distillates obtained from heating knots at both laboratories is given in Table 4. The compounds listed represent only those that could be positively identified by comparison of retention times and mass spectral data, or that gave excellent matches to spectral data in MS libraries. Most of the compounds present in small proportions have not been identified and many of these are no doubt oxidation products of the compounds present in the green tissues.

Because yields of monoterpenes in the distillates were low as compared with the amounts of these compounds present in the knots, we extracted two knots

TABLE 4.
Compounds Found in Methylated Distillates Obtained from Heating Knots

Compound	Identification
Tricyclene	RT, MS, Authentic Compound
α-Pinene	RT, MS, Authentic Compound
Camphene	RT, MS, Authentic Compound
β-Pinene	RT, MS, Authentic Compound
Myrcene	RT, MS, Authentic Compound
α-Phellandrene	MS, Library
β-Phellandrene	MS, Library
γ-Phellandrene	MS, Library
γ-Terpinene	RT, MS, Authentic Compound
4-Methyl-1-(1-methylethyl)- 3-cyclohexen-1-ol	MS, Library
Sylvestrene	MS, Library
α-Terpinolene	MS, Library
p-Cymene	RT, MS, Authentic Compound
Limonene	RT, MS, Authentic Compound
Δ-4-Carene	MS, Library
γ-Terpinene	RT, MS, Authentic Compound
α-Terpinene	RT, MS, Authentic Compound
Fenchyl alcohol	RT, MS, Authentic Compound
Camphene hydrate	MS, Library
Borneol	RT, MS, Authentic Compound
4-terpineol	RT, MS, Authentic Compound
Linalyl propionate	MS, Library
α-Terpineol	RT, MS, Authentic Compound
γ-Terpineol	MS, Library
4-Allylanisole	RT, MS, Authentic Compound
1-methyl-3-(1-methylethyl)-benzene	MS, Library
Endo-bornyl acetate	MS, Library
Methyl eugenol	RT, MS, Authentic Compound
Methyl pimerate	RT, MS, Authentic Compound
Methyl isopimarate	RT, MS, Authentic Compound
Methyl dehydroabietate	RT, MS, Authentic Compound
Methyl abietate	RT, MS, Authentic Compound
Methyl neoabietate	RT, MS, Authentic Compound

that had been heated at 120°C for 4 h. After drying at these conditions, an average of 35% of dichloromethane-soluble material was recovered from the heated knots. GC-MS of the methylated extract showed that in proportion to the amounts of resin acids, very little monoterpene remained in the knot even after heating at 120°C for 4 h. However, because the total amount of extract is so high, these small proportions could add significantly to the total amount of VOC emissions from lumber or veneer drying. The major identified products remaining were: α-pinene, camphene, β-pinene, Δ^3-carene or α-phellandrene, α-terpinene, *p*-cymene, limonene, γ-terpinene, β-phellandrene, borneol, terpinen-4-ol, 4-allylanisole, methyl sterate, dimethyl pinosylvin, methylpimarate, methyl sandaracopimarate, methyl isopimarate, methyl palustrate, methyl pinosylvin, methyl dehydroabietate, methyl abietate, and methyl neoabietate.

Myrcene, terpinolene, α-terpineol, 4-allylanisole, and methyl pinocembrin were present in unheated knots but were not found in the heated knots. The absence of these compounds in heated knots suggests that thermal oxidation of these compounds within the knot during drying is important.[20] This observation was supported by our finding a number of compounds in the knots that had been heated at 120°C that were not found in the unheated knots. Those compounds included α-terpinene, *p*-cymeme, γ-terpinene, camphor, and terpinen-4-ol as well as many as yet unidentified products.

Although the levels of volatile compounds in knots have the potential to dramatically increase VOC emissions in drying southern pine lumber, significant proportions of these compounds do not seem to find their way through the comparatively dense structure to enter the air stream. It seems that much of the volatile material is trapped within the knot and undergoes thermal rearrangement or oxidation before that can enter the air stream as judged from the composition of the dichloromethane-soluble materials identified before and after drying and the comparatively low yields recovered.

Knot Volume as Compared to VOCs from Lumber Dried in an Experimental Kiln

The above results suggest that, despite their potential to contribute

strongly to VOC emissions, knots may not be as important to the VOCs associated with drying lumber as one would have predicted on the basis of the amount of dichloromethane-soluble extractives in knots. However, the amounts of VOCs that are obtained from knots are still far greater than from wood. Therefore, we examined the effect of knots on VOC emissions using a small experimental kiln (Fig. 1) and measured the VOCs emitted using a total hydrocarbon analyzer. The number of knots per kiln charge ranged from 0 to 15 and knot volumes ranged from 0 to 1420 cm^3 (i.e., 0 to 5.0% of lumber volume). VOC emissions ranged from 2.86 to 4.25 lb of carbon/dry ton (0.15 to 0.21%) of lumber. GC-MS of the condensate oil collected between 4 and 8 h of kiln drying showed that monoterpenes, including α-pinene, β-pinene, and limonene together with 4-allylanisole, made up about 90% of the material collected in a cold trap. Small amounts of the methyl ester of dehydroabietic acid were detected in the methylated product. The above results are consistent with reports by some southern pine sawmills that have indicated VOC emissions of approximately 3 lb of carbon per 1,000 board feet (MBF) of lumber dried.

The actual dimension of nominal rough sawn green 2 in x 6 in lumber would be expected to be about 1.7 in thick, 5.8 in wide and 12 in long which corresponds to 1940 cm^3 and, at an average specific gravity of 0.48, would weigh 931 g or 2.05 lb dry weight. Therefore, VOC emissions at a rate of 3 lb/MBF of lumber would be equivalent to an emission rate of about 3 lb per ton of lumber dry weight or 0.15% on a weight basis. If the VOC emissions were similar to those found in heating clear sapwood at 100 to 120°C for 4 h (Table 2), we would have expected to find VOC yields of only about 1.1 to 1.2 lb/ton (0.055% of identified products) of lumber.

Under the same heating conditions (averaging data for 100 and 120°C for 4 h), we identified products in the distillate amounting to 0.36% of the knot weight which would be equivalent to 7.2 lb/ton of knot material. Knots have a specific gravity of approximately 1.0 or twice that of wood. Therefore, 5% of knots on a volume basis would be equivalent to approximately 10% on a weight basis. Under the above assumptions, the amount of VOC emissions from lumber

containing 5% of knot volume would be predicted to be (1.1 lb x 90% by weight = 0.99 lb from wood) + (7.2 lb x 10% by weight = 0.72 lb from knots) for a total of 1.71 lb of volatiles emitted per ton (or Mbf) of lumber. The proportion of distillate derived from knots at 5% of lumber volume would be predicted to be 42% of the total VOCs using this data. This calculated yield of VOCs (1.71 lb/MBF) is about half that actually recovered in the experimental kiln study (3.29 lb/MBF).

There are several reasons why predictions of the amount of VOC emissions based on the yields found in heating sapwood and knot material might seriously underestimate the actual about of VOC emissions measured in drying the lumber. Most obvious is that the yields documented in Table 3 represent heating periods of only 4 h in comparison with the 19 h of heating at a dry-bulb temperature of 115°C. Heating knots at 140°C for 19 h gave condensate oils that were close to 10 times the amounts (Table 2) that were used in the above calculations. Also, the yields shown in Tables 2 and 3 represent only the amounts of compounds that were actually identified as major constituents of the distillate. The many compounds found in small proportions of the total distillate that are not included in Table 3 could add up to significantly higher total yields of volatile emissions. The presence of heartwood was not considered in those computations.

The Effect of Heartwood on VOCs from Lumber Drying

An important source of VOC emissions from drying lumber may be heartwood because much higher amounts of terpenes are found in heartwood than in sapwood.[7,8] The amounts of volatile compounds in the dichloromethane-soluble extracts of sapwood, heartwood, and knots isolated at different positions in the tree are in Table 5. The dichloromethane-soluble extracts of sapwood samples selected throughout the length of the tree ranged from 0.051 to 0.64% and averaged 0.31% of dry tissue weight. There was no observable trend in concentration of VOCs with height in the tree. By comparison, the heartwood samples ranged from 0.66 to 2.6% of the dry tissue weight. The average

TABLE 5.

Amounts of Volatile Compounds[a] in Sapwood, Heartwood, and Knots From Various Heights in a 45-Year Old Loblolly Pine Tree

Sample Location	Sapwood	Heartwood	Knots
Height in tree (ft)	**Percent of Extractive Free Dry Tissue**		
0-10	0.28	0.67	3.66
0-10	0.29	0.86	4.52
0-10	0.21	0.66	4.60
10-20	0.64	2.11	2.66
10-20	0.28	1.87	2.99
10-20	0.12	1.13	2.52
20-30	0.05	2.31	3.12
20-30	0.70	2.62	2.71
20-30	0.47	1.66	2.99
30-40	0.17	1.09	no samples
30-40	0.35	1.05	no samples
30-40	0.14	2.07	no samples
Ave.	0.31	1.51	3.31
COV (%)	63	43	22

[a] Compounds measured in this analysis were α-pinene, camphene, β-pinene, limonene, borneol, fenchyl alcohol and 4-allylanisole that make up the majority of the volatile compounds in the tissue prior to drying. The resin and fatty acids and other high boiling point compounds in the dichloromethane-soluble extracts are not included in these data.

concentration of VOCs throughout the length of the tree was 1.51%, or approximately 5 times, the amounts found in the sapwood. Interestingly, the lowest concentrations were found at the base of the tree. As was found in the previous work on knots, the amounts of volatile compounds found in knots ranged from 2.52 to 4.60% with an average of 3.31% of the tissue dry weight. Despite the fact that approximately 30% of the knot tissue was soluble in dichloromethane, only about one-tenth of that extract is made up of volatile compounds; the majority is due to diterpene resin acids. Nevertheless, the amounts of volatile terpenes in knots were 10.7 and 2.2 times the amounts found

in sapwood or heartwood, respectively (Table 5). In an attempt to simulate the drying conditions used in the experimental kiln, we heated samples of sapwood, heartwood, and knots at 115°C for 20 h and collected the volatile oils at heating times of 0-4, 4-8, and 8-20 h of heating. Those results (Fig. 3) showed that the amounts of volatile oils produced from heating knots (3.40% of oven dry weight) were far higher than predicted from the data shown in Tables 2 and 3. Nearly as much volatile material was recovered from the heartwood (2.01% of oven dry weight) as from knots. The amount of volatile material collected from heating sapwood (0.22% of oven dry weight) was only about one-tenth of the amount obtained from heartwood or knots. GC analysis indicated that the oil layer from each of the tissues comprised primarily α-pinene, β-pinene, limonene, and other monoterpenes.

If we assume that the kiln charge averaged 66% by weight of sapwood, 30% by weight of heartwood and 4% by weight of knots (2% of knots on a volume basis) and VOC emissions at the rates shown in Figure 3, then the total VOC emissions would then be: (2,000 lb/ton x 66% sapwood x 0.22% VOC) = 2.90 lb from sapwood, (2,000 lb/ton x 30% heartwood x 2.1% VOC) = 12.60 lb from heartwood, and (2,000 lb/ton x 4% knot weight x 3.4% VOC) = 2.72 lb from knots for a total of 18.24 lb of VOC/ton (or MBF) of lumber dried. Using the amounts of VOC emissions measured in the same experiment shown in Figure 3, we would predict 6.94 lb of VOCs/ton (or MBF) assuming no heartwood and 2% knot volume. Because this is actual weight recovered and not expressed as carbon only, this latter estimate is not far from the results of the experimental kiln trials. Nevertheless, it seems likely that much of the variation that was not accounted for by the presence of knots is likely due to variations in the amount of heartwood present in the lumber dried.

CONCLUSIONS

Our hypothesis that the volatile compounds in knot extractives can contribute substantially to the VOC emissions in drying southern pine lumber or veneer, while not as significant as first thought on the basis of total extract yields,

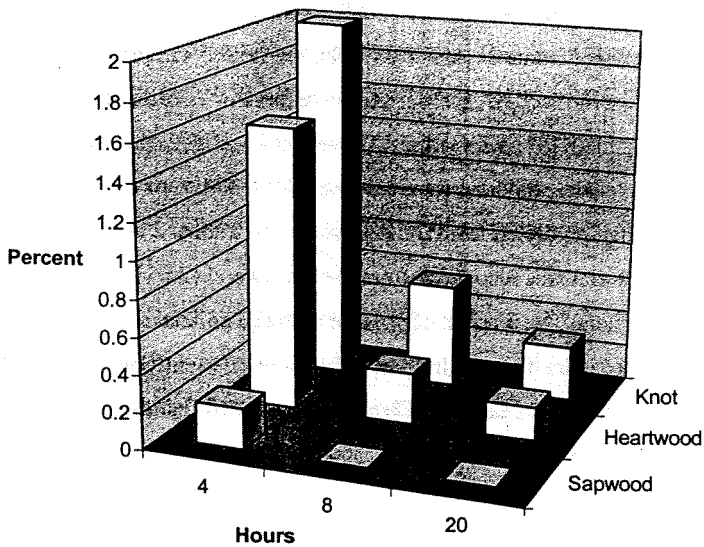

FIGURE 3. Distribution of Volatile Oils Obtained from Sapwood, Heartwood, and Knots Heated at 115°C for 20 h.

still seems to have held true. On the basis of the amounts of VOC emissions obtained from clear sapwood and knot materials heated for 4 h at 120°C, we predict that at least 44% of the VOCs are derived from knots at a relative volume to clear sapwood of 5% of the lumber. However, a linear regression of VOC emissions compared to the volume of knots and the number of knots gave R^2 values of only 0.57 and 0.51, respectively. In an effort to explain that low correlation coefficient, we examined the amounts of volatile terpenes in heartwood and heated sapwood, heartwood, and knots under time/temperature conditions that paralleled the conditions used in drying lumber in the experimental kiln. Heartwood VOC emissions were nearly the same amount as were obtained from knot tissue. Therefore, the presence of different amounts of heartwood in a kiln charge would cause wide variations in the amount of VOCs emitted.

The results obtained from the drying tube experiments no doubt over estimate the amounts of high boiling point compounds that might be released as aerosols. However, those compounds are important to the formation of "blue haze" and further studies of the amounts of those compounds in emissions from lumber and particularly veneer drying operations are warranted.

ACKNOWLEDGMENTS

This work was funded by the USDA Competitive Grant Program for Wood and Wood Fiber, Grant No. 96-35103-3772. Approved for publication as Journal Article No. FP159 of the Forest and Wildlife Research Center, Mississippi State University.

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