BOUND CHLORINATED RESIDUE IN CHLOROPICRIN-TREATED DOUGLAS-FIR[1]

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ABSTRACT

Douglas-fir wafers exposed to chloropicrin vapors, then aerated and heated or extracted with acetone, were analyzed under a scanning electron microscope equipped with an energy dispersive X-ray analyzer. Chlorinated residues appeared to be most concentrated in the middle lamellae and in areas where wood extractives were located, which indicates that the residues were selectively binding to phenolic materials. Thin layer chromatography of acetone extracts of the treated wood suggested that chlorinated residues were binding to extractives, particularly to a portion of the phenolic extractive dihydroquercetin. Analysis of a mixture of vanillin (a phenolic lignin derivative) and chloropicrin showed the presence of two other compounds. Mass spectroscopy tentatively identified these as CCl_3-vanillin and NO_2-vanillin. This identification suggests that the chloropicrin molecule was fragmented and that the two components were chemically linked to the vanillin molecule at an unspecified point. The data suggest an explanation for the presence of a phenolic-bound chlorinated residue in chloropicrin-treated wood.

Keywords: Douglas-fir, vanillin, chloropicrin, residue, fumigant, decay-control, energy dispersive X-ray analysis, mass spectroscopy, thin-layer chromatography.

INTRODUCTION

Volatile fumigants have been used commercially to control wood decay fungi in transmission poles since the early 1970's (Graham and Corden 1982). One of their main advantages as wood preservatives is that fumigant (gas) molecules can move through the pits without surface tension interference (Beall and Wang 1974) and can rapidly diffuse through the wood structure. However, if the fumigant is not bound, and if forces such as surface tension that serve to retain conventional liquid preservatives are not active, the fumigant may also readily diffuse out of the wood.

It is known that fumigants will bond to organic matter and clays in the soil (Gersti et al. 1977; Goring and Haymaker 1972) and that low levels of many fumigants are retained in stored grains after aeration (World Health Organization 1971). Low levels of chloropicrin residues in stored grain products after fumigation

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have been reported, but no quantitative data are available (Food and Agriculture Association/World Health Organization 1965). Volatile fungitoxic residues have been found in chloropicrin-treated wood as long as 13 years after treatment (Graham and Corden 1982), and recent work (Goodell et al. 1985) has shown that a nonvolatile chlorinated residue is present in Douglas-fir after chloropicrin treatment. The purpose of the research presented here was to determine if chlorinated residues are bound to chloropicrin-treated Douglas-fir wood, and if so, to determine the mechanism for the binding.

MATERIALS AND METHODS

Energy dispersive X-ray analysis

Scanning electron microscopy (SEM) was used in conjunction with energy dispersive X-ray (EDX) analysis to observe the location of elemental chlorine in the microstructure of chloropicrin-treated Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco]. In one treatment, 45 × 90 × 5 mm wafers were exposed to a saturated atmosphere of chloropicrin for 35 weeks, aerated for 19 weeks, and extracted with acetone or heated to 115 C for 5 hours (Goodell et al. 1985). Some untreated control wafers were also extracted with acetone or heated to 115 C for 5 hours. In another treatment, one end of three 9 × 9 × 150 mm blocks was submerged in liquid chloropicrin for 2 weeks.

Following these treatments, transverse and radial surfaces were prepared for EDX analysis for chlorine. The treated wood was split to expose radial surfaces and razor- or microtome-sectioned to expose transverse surfaces. For sectioning, dry and slightly wetted wood initially were used because wet sectioning produced better surfaces for microscopy. Preliminary observations indicated that wet sectioning did not appear to affect retention of chlorine; therefore, the remainder of the sample surfaces were prepared by this method.

Thin-layer chromatography

Acetone extracts from the vapor-treated and control samples were analyzed by two-dimensional thin-layer chromatography (TLC) on silica gel plates sequentially developed in chloroform/methanol (96:4) and chloroform/ethyl acetate/formic acid (50:40:10) solvent systems. Chlorinated residues on the TLC plates were detected with a silver nitrate/bromophenol-blue spray reagent (Touchstone and Dobbins 1978).

Mass spectroscopy

For studying the reaction of chloropicrin with phenolic groups in wood, a model compound representative of the groups was needed. Because vanillin, a derivative of the lignin molecule, differs only in that the propyl side chain of the lignin monomer has been replaced by an aldehyde group, it should adequately represent many chemical reactions that lignin would undergo. For this reason, vanillin was used in a simple test designed to determine how chloropicrin may bind to the phenolic components in wood.

Approximately 5 mg of crystalline vanillin was mixed with 2 ml of reagent-grade chloropicrin. The mixture was allowed to react at room temperature (20–22 C) for 5–6 hours before analysis by gas chromatography/mass spectroscopy.

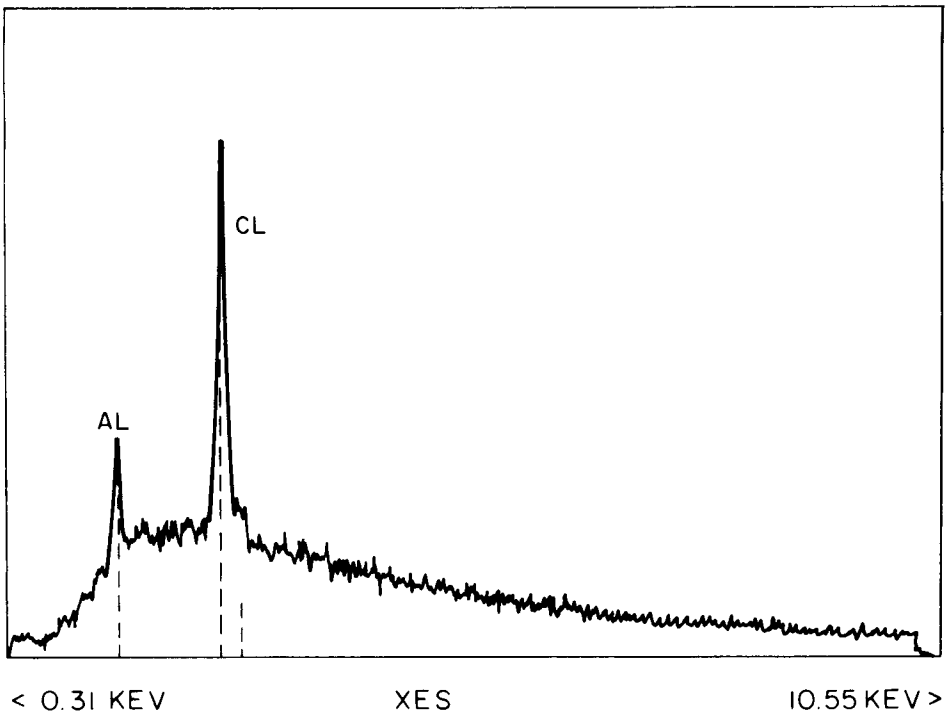

FIG. 1. An energy dispersive X-ray spectral scan of extracted or heated chloropicrin-treated wafers. Peak for aluminum is an artifact, contributed by the aluminum sample holder in the SEM chamber. Sample counting time was 200 seconds. The number of counts in the vertical scale was 256.

Chromatographic separation of the mixture was performed with a 10 ft by 2 mm I.D. pyrex column with a 7% OV 101 liquid phase coated on a 100/120 supelcoport support phase.

RESULTS AND DISCUSSION

Energy dispersive X-ray analysis

EDX analysis of all untreated wood samples showed no detectable chlorine, but in vapor-treated wafers, even those that had been extracted or heated, significant amounts were present (Fig. 1). Line scans across cell walls of vapor-treated samples showed that entire walls contained detectable amounts of elemental chlorine which tended to concentrate at the center in the middle lamella region (Fig. 2A, B). Caution must be exercised when analyzing objects as small as cell-wall layers with EDX; however, greater concentrations of chlorine were noted when scanning over cell corners where the middle lamellae are large enough for accurate EDX analysis.

Line scans across ray tissue of vapor-treated samples indicated that more chlorine was present than in the tracheid tissues (Fig. 2C). A spectral scan across adjacent ray parenchyma cells (Fig. 2D) showed large amounts of chlorine in the walls and on the interior surfaces of the ray cell walls. The later location is a site where phenolic heartwood extractives would be found most prevalently.

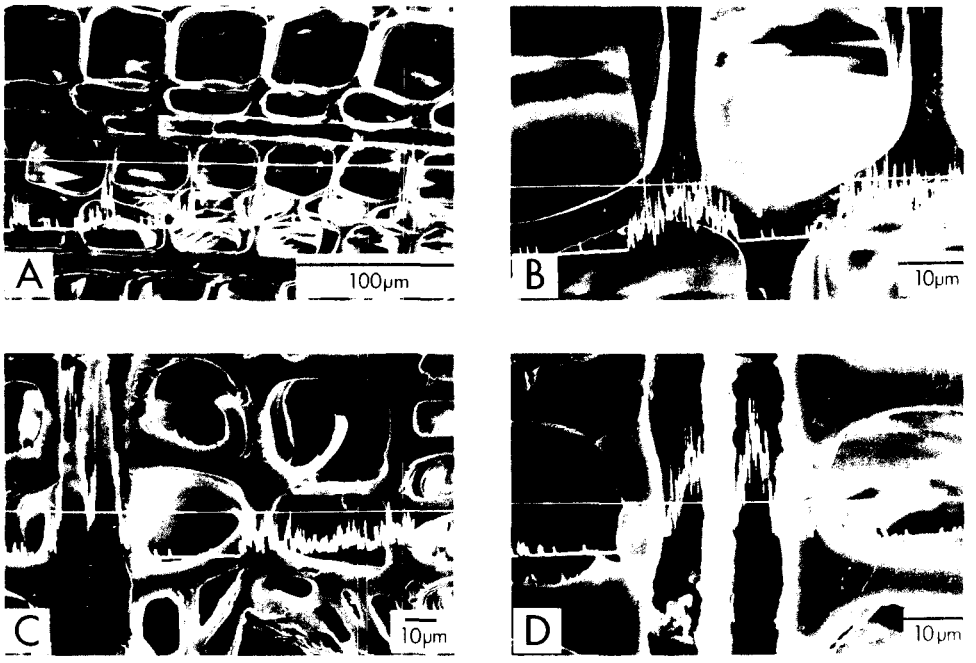

FIG. 2. Line scans for chlorine across the transverse surface of chloropicrin-treated samples. The upper straight line is the position of the line scan. Lower line peaks show the location of bound chlorine. (A) Heated sample with chlorine in tracheid cell walls. (B) Heated sample with higher concentrations of chlorine in middle lamellae. (C) Acetone-extracted sample with large concentrations of chlorine in ray cells and in the cell with included deposits. (D) Acetone-extracted sample with large amounts of elemental chlorine in the lumens of ray cells.

These data indicate that chloropicrin or chloropicrin breakdown products may selectively bind to lignin and to extractive material. As lignin is a complex phenolic material and as many extractives are phenolic, chloropicrin residues appear to be binding to the phenolic compounds in Douglas-fir.

EDX spectra of the wood blocks treated with liquid chloropicrin for 2 weeks showed no chlorine. There are two possible explanations. First, vapor-phase oxidation of chloropicrin may be required to form reactive degradation products that can bind to the wood. Liquid phase treatment that excludes most oxygen could limit the reaction. Second, the vapor phase treatment in this study was continued much longer than the liquid treatment. If binding of chloropicrin to wood is time-dependent, the amount of chlorine present in the liquid-treated wood may have been insufficient for detection by EDX analysis.

Thin-layer chromatography

Thin-layer chromatography of acetone extracts from the wafers in the chloroform/methanol solvent system showed that two substances (R_f 0.10 and 0.44) were eluted from the control-sample extract but only one (R_f 0.10) from the treated-sample extract. The eluted materials were not identified, but both could be distinguished from dihydroquercetin, an extractive in Douglas-fir wood, which did not move in this solvent system. When the TLC plates were then developed

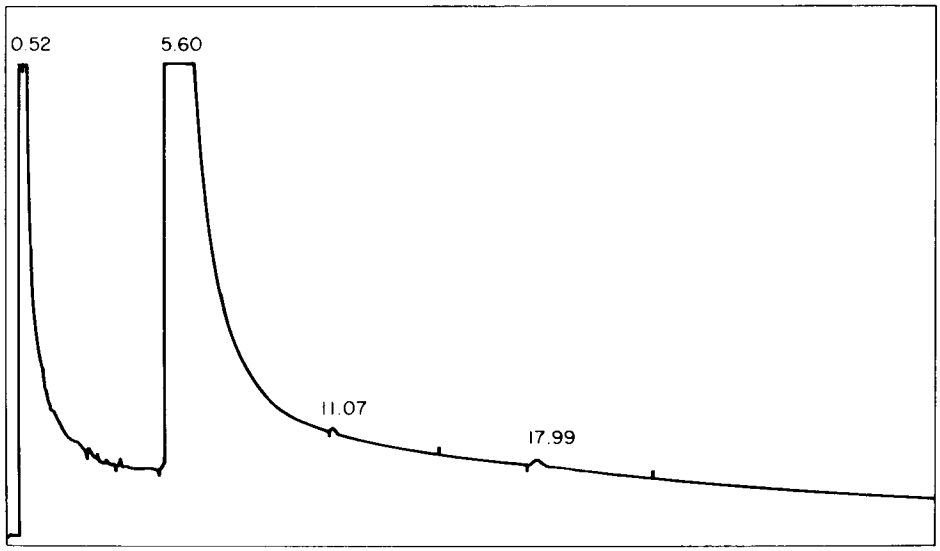

FIG. 3. Analysis of a reacted mixture of chloropicrin (retention time 0.52 min) and vanillin (retention time 5.60 min) by gas liquid chromatography. Reaction products are present at retention times 11.07 min and 17.99 min.

in chloroform/ethyl acetate/formic acid, a substance with the same R_f value as dihydroquercetin was eluted from the control, but only a faint trace of it was eluted from the treated-sample extract. A chlorine spray detector showed that none of the eluted materials was chlorinated. Nevertheless, chlorine was indicated at the baseline of the treated chromatogram. This suggests that chloropicrin may bind to one of the unidentified extractives from the control-sample extract (R_f 0.44 in chloroform/methanol) and, probably, to a large portion of the dihydroquercetin in the wood, thereby inhibiting mobility of the extractives in the solvent systems tried on the TLC plates.

Mass spectroscopy

Two small peaks beyond the large peaks of chloropicrin and vanillin were present in the gas chromatograph analysis of the reaction mixture (Fig. 3). The two small peaks occupied approximately 0.1% of the area of the chloropicrin peak. When unreacted chloropicrin and vanillin were injected simultaneously into the gas chromatograph/mass spectrometer, only peaks for the parent compounds were present, indicating that the reaction products were not artifacts produced in the injection port.

Mass spectral analysis of the first unidentified peak in Fig. 3 (retention time = 11.07 min) yielded prominent isotopic fragments of 197, 180, 152, and 151. The 197 peaks would correspond to the vanillin ion (152 mass units minus one proton = 151) and an NO_2 fragment (46 mass units) from chloropicrin. The 180 and 152 peaks can be explained by the sequential loss of ·OH (17 mass units) and CO (28 mass units) from the vanillin portion of the parent ion. These data indicate that the compound is nitrovanillin. Analysis of the second unidentified peak in Fig. 3 (retention time = 17.99 min) yielded prominent isotopic fragments clustered

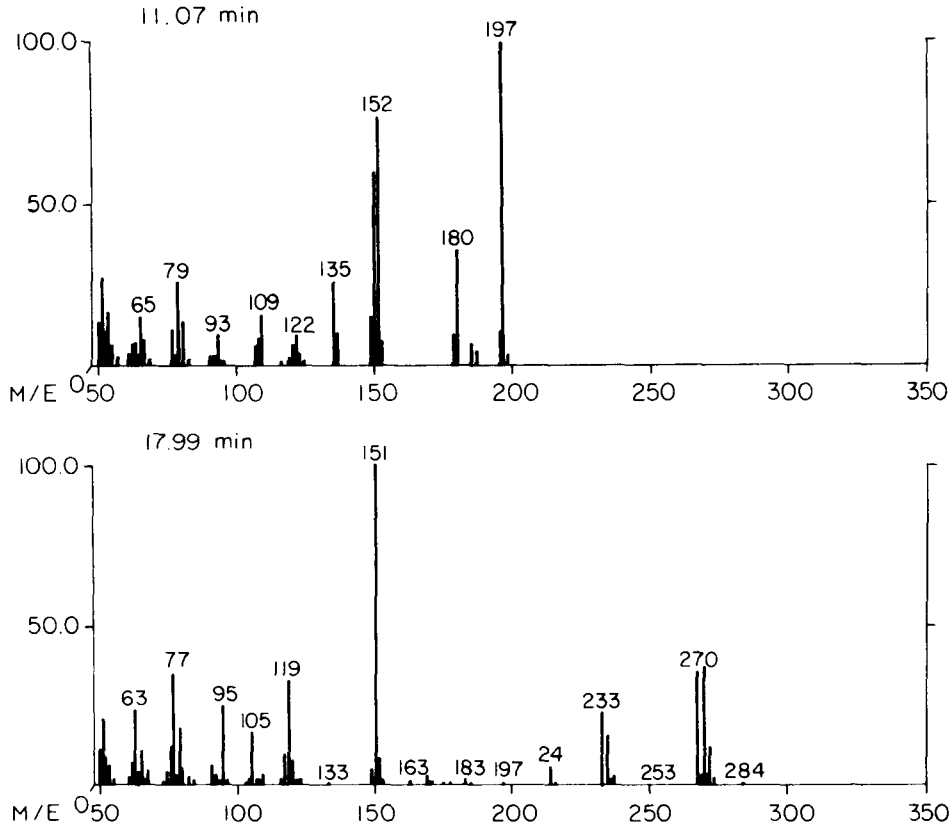

FIG. 4. Mass spectrograph of chloropicrin/vanillin reaction products at 11.07 min and 17.99 min (Fig. 3). Parent ion mass = 197 and 270, respectively.

at 268, 270 and 272; 233 and 235; and at 151. The ion peak at 151 would again correspond to the vanillin ion minus a proton. The remaining peak clusters display characteristic patterns for two-chlorine compounds (*m/e* 233 and 235), and three-chlorine compounds (*m/e* 268, 270, and 272) due to the distribution of ^{35}Cl and ^{37}Cl in nature. The ion at 233 corresponds to the loss of a ^{35}Cl from the parent ion at 268, and the ion at 151 corresponds to the loss of two additional chlorines plus a carbon. This indicates that the remaining fragment of chloropicrin $\cdot CCl_3$ can bond to the vanillin ion to form trichloromethylvanillin.

The breakdown of chloropicrin into NO_2 and CCl_3^+ transition states has been proposed to explain the mechanism for chloropicrin breakdown to phosgene and nitrosyl chloride (Moilanen et al. 1978), but evidence of the existence of these products is lacking. Our data indicate that a small portion of chloropicrin was broken down in the reaction mixture and that the breakdown products NO_2 and CCl_3^+ were covalently bound to the vanillin molecule. This reaction could be the mechanism for the attachment of chloropicrin residues to phenolic materials in treated wood, which would explain the distribution of elemental chlorine observed with EDX analysis and the presence of chlorinated extractives on TLC plates.

CONCLUSIONS

Chlorinated residue in wood after treatment with chloropicrin appears to be associated with lignin and extractive components. The specificity of the association suggests that the residue is not randomly held in the wood by hydrogen bonds or other weak forces, but is covalently bound to sites on wood components that are primarily phenolic. Mass spectroscopy indicates that the chloropicrin molecule can fragment and react with vanillin, a phenolic lignin derivative, to produce a chlorinated phenolic material. This suggests a possible mechanism for the selective binding of chlorinated fragments from the chloropicrin molecule to lignin and phenolic extractives in wood.

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