FUNGAL DECAY RESISTANCE OF LOBLOLLY PINE OR SWEETGUM REACTED WITH AQUEOUS POTASSIUM IODATE[1]

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ABSTRACT

In this study, we investigated the protection of wood based on complexation of biocides with wood. We found that loblolly pine and sweetgum wood blocks soaked in aqueous potassium iodate for 1 day resisted decay by brown- and white-rot fungi even after 2 weeks of water leaching. Threshold retentions of iodate for *Gloeophyllum trabeum* were 0.5 and 1% by weight of iodate solution in wood for unleached and leached blocks, respectively. For *Coriolus versicolor*, the threshold retention was 0.1% for both unleached and leached blocks. Retention of iodate in leached wood ranged from 21 to 73% that of unleached wood. Retentions of iodate were higher in loblolly pine than in sweetgum. Infrared spectrum of iodate-reacted wood indicated that iodate forms complexes with cell-wall polymers of wood, probably with cis diols of hemicelluloses and lignin. However, the intensity of this absorption was weak. Also, a small amount of oxidation of lignin in wood was found.

Keywords: Potassium iodate, complexation, fungal decay resistance, *Gloeophyllum trabeum, Coriolus versicolor,* loblolly pine, sweetgum.

INTRODUCTION

Complex formation between chromates or copper (II) and cell-wall polymers of wood along with deposits of the less water-soluble compounds, copper (II) arsenate and copper (II) chromate, in the cell lumen of wood accounts for the permanence and effectiveness of chromated copper arsenate (CCA) as a wood preservative. Complex formation between chromates and lignin model compounds has been reported (Pizzi 1979). This finding led to the assumption that chromates in wood may form complexes with diols of lignin and hemicellulose. Because chromate complexation of wood plays an important role in the permanence of CCA preservatives in wood (Fahlstrom et al. 1967; Wallace 1968; Ochrymowych and McOrmond 1978; Pizzi 1982; Gjovik and Gutzmer 1985), we investigated other biocides that can form complexes with wood. In a previous study, we found that periodates could form complexes with diols of cell-wall polymers in wood. The resulting periodate-complexed wood resisted water leaching as well as fungal degradation (Chen and Rowell 1989).[2] Iodate, like other anions including phosphate, nitrate, arsenate, thiosulfate, chromate, sulfate, and selenate, has reduced oxidative phosphorylation in plant mitochondria (Miller et al. 1975) and has sterilized water (Heuston 1974).

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This investigation determined the fungal decay resistance of wood reacted with potassium iodate and studied the reaction of potassium iodate with wood.

MATERIALS AND METHODS

Reaction of wood with aqueous potassium iodate

Loblolly pine *(Pinus taeda* L.) or sweetgum *(Liquidambar styciflua* L.) sapwood blocks (1.9-cm cubes) were selected according to American Society for Testing and Materials (ASTM) standards (ASTM 1990).

The blocks were placed in a desiccator under vacuum for 1 h at 2.27 to 3.33 KPa and then were impregnated with iodate solution. Each block was then soaked for 24 h in one of six concentrations of aqueous potassium iodate. The iodate solution was prepared using distilled water. The concentration levels were 1.0, 0.5, 0.1, 0.05, 0.025, and 0.01% by weight. After soaking, seven blocks per treatment were dried in a chemical fume hood for 1 day and then conditioned at 27 C and 30% relative humidity (RH) for 3 weeks. Another seven blocks per treatment were leached in 350 ml of distilled water, which was changed each day for 2 weeks. After leaching, the leached blocks were conditioned at 27 C and 30% RH for 3 weeks.

Decay test

Soil-block fungal decay tests were conducted according to ASTM standards (ASTM 1990). *Gloeophyllum trabeum* (Pers. : Fr.) Murr. (Madison-617), a brown-rot fungus, was used with loblolly pine blocks, and *Coriolus versicolor* (L. : fr.) Quel. (Madison-697), a white-rot fungus, was used with sweetgum blocks. Five replicate blocks from each treatment and five control blocks were tested for decay resistance over a 12-week period. The extent of fungal attack was determined by weight loss. Solution retention concentration that resulted in weight loss by decay of ≤ 2 percent was considered to be the threshold retention.

Infrared analysis

Infrared spectra of one of four loblolly pine sapwood blocks (1.9 by 1.9 by 0.64 cm) reacted with 7% aqueous solution of potassium iodate (50 ml) for 2 days was recorded on a Nicolet[3] (Madison, WI) model 6000 Fourier Transform infrared spectrophotometer using KBr pellets. Each of the iodate-reacted blocks was leached in 50 ml of distilled water for 3 days. One of the leached blocks was ground in a Wiley mill and wood particles that passed through a 60-mesh (250 micron) screen were used to prepare KBr pellets.

Reaction of D-mannopyranose with potassium iodate

D-mannopyranose (7.44 g, 40 mmol) and potassium iodate (8.56 g, 40 mmol) dissolved in distilled water (100 ml) were stirred at room temperature for 2 days. Thin layer chromatographic plates were used to monitor the reactions. These thin-layer plates (precoated silica gel sheets with fluorescence indicator F-254; methanol : H_2O, 7:3 v/v) showed the following R_f values: iodate-D-mannopyranose complex, 0.77; potassium iodate, 0.85; and D-mannopyranose, 0.45. The complex formation between D-mannopyranose and potassium iodate, as indicated in the thin layer plates, was completed in 2 days. After the reaction, ethanol (200 ml) was added to the solution, and the white precipitates were recovered by filtration and dried in a vacuum to give a white solid (8. 1 g; 50% yield). The white solid was characterized by infrared spectra using KBr pellets.

RESULTS AND DISCUSSION

Reaction and decay tests

Wood reacted with aqueous potassium iodate resisted decay by brown- and white-rot fungi at low solution concentrations. Thresh-

[3] The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

TABLE 1. *Average weight loss of wood treated with potassium iodate after a 12-week exposure to fungi in a soil block test.*

Solution concen-tration (%)	Retention (%, w/w)[a]		Weight loss (%)[b]			
			G. trabeum		*C. versicolor*	
	Loblolly pine	Sweetgum	Unleached	Leached	Unleached	Leached
1.0	1.35	1.58	1.0 (0.2)	1.2 (0.8)	0.9 (0.1)	0.2 (0.3)
0.5	0.67	0.77	1.7 (0.7)	7.3 (5.1)	0.7 (0.2)	0.5 (0.4)
0.1	0.13	0.15	24.2 (10.2)	39.6 (2.7)	1.0 (0.3)	0.5 (0.5)
0.05	0.06	0.08	43.5 (3.8)	54.0 (4.8)	4.9 (2.3)	8.6 (11.1)
0.025	0.03	0.04	49.7 (3.9)	52.2 (5.1)	21.1 (4.2)	21.7 (6.6)
0.01	0.01	0.02	58.4 (13.0)	52.9 (7.6)	30.9 (1.9)	38.8 (6.1)
Control	N/A	N/A	61.9 (4.9)	—	44.1 (3.8)	— (6.1)

[a] Percent iodate in wood (w/w) before leaching; mean of 10 replicates including five unleached and five leached blocks.
[b] Mean of five replicates. Values in parentheses are standard errors.

old retentions with *G. trabeum* were 0.5 and 1% by weight of iodate solution in wood for unleached and leached blocks, respectively. With *C. versicolor*, the threshold retention was 0.1% for both unleached and leached blocks. Leaching of the iodate-reacted blocks did not decrease decay resistance to *C. versicolor* but did decrease decay resistance to *G. trabeum* in the solution concentration range from 0.5 to 1% (Table 1).

Chemical analysis of iodine in wood reacted with aqueous potassium iodate revealed that between 21 and 73% iodate was retained in wood even after 2 weeks of water leaching. The retention of iodate in loblolly pine was higher than in sweetgum. For example, loblolly pine sapwood soaked in potassium iodate solutions at 0.01, 0.1 and 1% by weight concentration levels for 1 day retained 60, 73, and 38% iodate, respectively after leaching. Sweetgum sapwood retained only 53, 32, and 21% iodate at the same concentration levels after leaching (Table 2). The higher retention of iodate in loblolly pine may be attributed to its higher glucomannan content– 11% as compared to 3.6% for sweetgum (Rowell 1984). The ability of D-mannopyranose to complex with iodate, as shown in this study, indicated that glucomannan in wood may complex with iodate.

The retention of iodate in leached wood may indicate that potassium iodate was able to react with wood in 1 day to form stable complexes with cell-wall polymers of wood. Therefore, the reaction of potassium iodate with wood was not merely a deposition of iodate in wood. Rather, it involved bond formation between iodate and wood polymers, particularly the more accessible and configurationally more favorable diols of hemicelluloses and lignin. The C-2 and C-3 vicinal diols of D-mannopyranose containing hemicelluloses were in cis configuration, which is favorable for the bonding of iodate to these polysaccharides. The cis diols and alpha-hydroxy keto groups in lignin were also favorable for the bonding of iodate to lignin polymers. The moderate-to-high retentions (38 to 73%) (Table 2) of iodate in wood even after water leaching could explain why the leached blocks were as effective as the unleached blocks in resisting fungal decay.

TABLE 2. *Effect of water leaching on iodine content of potassium iodate-reacted wood.*

Solution concen-tration (%)	Iodate retention in wood before leaching (%, w/w)	Iodine content[a] after leaching (%, w/w)	Iodate retained in wood after leaching (%, w/w)
Loblolly pine			
0.01	0.010	0.0060	60
0.1	0.10	0.074	73
1.0	1.08	0.41	38
Sweetgum			
0.01	0.010	0.0053	53
0.1	0.11	0.036	32
1.0	1.12	0.23	21
Control	<0.0002		

[a] Chemically analyzed by the Galbraith Laboratories, Inc., Knoxville, TN.

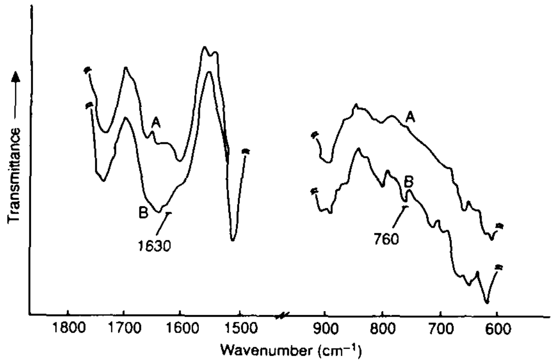

FIG. 1. Infrared spectra of wood reacted with potassium iodate. (A) control, (B) 1.2% iodine content.

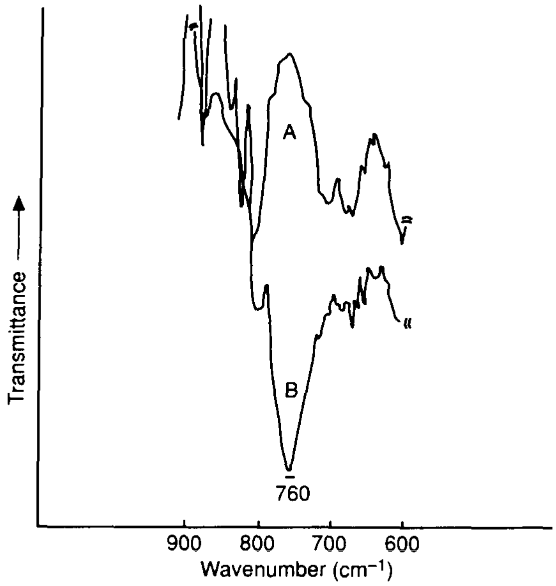

FIG. 2. Infrared spectra of D-mannopyranose reacted with potassium iodate. (A) D-mannopyranose, (B) D-mannopyranose-iodate complex.

The decay data suggested that decay protection in wood that has been reacted with iodate may be attributed to the release of iodate from wood. The hydrolytic and oxidative nature of fungal degradation of wood caused iodate to release from wood. Iodate may then act as a toxicant to inhibit the enzymes of wood-degrading fungi. The toxicity ofiodo compounds, including iodo-sulfonamide and periodates, to wood decay fungi has also been reported (Chen 1994; Chen and Rowell 1989). These iodo compounds in general are more effective in inhibiting the white-rot fungus, *C. versicolor,* than the brown-rot fungus, *G. trabeum.*

Decay protection based on substrate modification (the inability of the enzymes of wood-decay fungi to metabolize the modified wood substrate) as a result of complexation of iodate with wood polymers may not play a role here. Iodate in wood only forms complexes with D-mannopyranose containing hemicelluloses and diols of lignin. Therefore, cellulose and hemicelluloses, other than D-mannopyranose-containing polysaccharides, in wood remain open to attack by the brown-rot fungi, and these attacks are independent of the iodate concentration in wood if decay protection is based on substrate modification. The decay data showed that threshold retention of iodate was 0.5% and 1% to *G. trabeum* for unleached and leached blocks, respectively. This indicated that toxicity rather than substrate modification played an important role in fungal decay protection.

Infrared analysis

Wood reacted with 7% aqueous potassium iodate after water leaching contained 1.2% iodine, and the infrared absorption showed complex formation (760 cm^{-1}) between wood and iodate (Fig. 1B). This absorption was attributed to an iodate ion being coordinated to polymers (Socrates 1980). This indicated that the diols of hemicelluloses or lignin in wood may form complexes with iodate. However, the intensity of this absorption was weak because only 1.2% iodine was retained in wood. A small increase in carbonyl absorption at 1,630 cm^{-1} was probably related to the oxidation of phenolic hydroxyl groups of lignin by iodate. The oxidation of phenol by iodate has been reported (Scharma 1973).

Complexation of D-mannopyranose with potassium iodate

Infrared absorption of the complex between D-mannopyranose and potassium iodate showed a characteristic absorption. The absorption at 760 cm^{-1} was attributed to the coordination of iodate with D-mannopyranose (Socrates 1980). The intensity of this absorption was very strong (Fig. 2B).

Complex formation between potassium iodate and D-mannopyranose indicated that complexes between iodate and wood take place.

CONCLUSIONS

Blocks soaked in low concentrations of potassium iodate solutions for 1 day resist decay by brown- and white-rot fungi even after 2 weeks of water leaching. Threshold retentions with *G. trabeum* are 0.5 and 1% by weight for unleached and leached blocks, respectively. With *C. versicolor*, threshold retention is 0.1% by weight for both unleached and leached blocks.

The fact that iodate complexes form in wood and are retained even after two weeks of water leaching explains why leached blocks were as effective as unleached blocks in resisting fungal decay. Iodate retentions, which ranged from 21 to 73%, are higher in loblolly pine than in sweetgum.

Complex formation between D-mannopyranose and iodate indicates that complexes between iodate and cis diols of wood, particularly the cis diols of mannose-containing hemicelluloses or lignin, take place.

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