NATURAL PRODUCTS IN WOOD PRESERVATION

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INTRODUCTION

The main conventional wood preservatives - CCA, pentachlorophenol and creosote - are coming under pressure due to toxicity concerns. This is not due to these materials being particularly hazardous; treated wood in use has an enviable safety record. The problem lies with disposal of treating plant residues and unused treated wood. Waste materials containing CCA, pentachlorophenol and creosote have been classified by the EPA as being hazardous wastes. This has greatly increased the costs associated with disposing of treating plant residues. There is also growing consumer awareness of potential hazards associated with treated wood, particularly the arsenic in CCA and dioxin contamination of pentachlorophenol. It is clear that the development of non-hazardous wood preservatives is in the best interests of both the producers and consumers.

One approach to developing lower toxicity wood preservatives is to use natural chemicals. Of course, using natural products does not guarantee the safety of the final product. The same toxicity criteria imposed on synthetic chemicals would still need to be passed. There could be advantages, however, in the biodegradability of wastes and consumer acceptance. Home use of treated lumber for decks and other applications is a very important and growing portion of the market. The consumer appeal of a new preservative system could have a considerable influence on its competitiveness with conventional systems and other new preservatives. A formulation based on natural products could be more acceptable than a wholey synthetic system. An ongoing interest in our laboratory is to develop an understanding of how trees protect themselves from decay organisms. The ultimate goal of this work is to develop wood preservative systems based on how nature preserves wood.

WOOD PRESERVATION AS TREES DO IT

Trees must deal with many of the same wood decay problems that wood-in-use is exposed to. The roots and lower part of the stem are in contact with the soil, exposed to the variety of wood-destroying

fungi and insects found there. The ability of roots to survive with little apparent damage in high termite hazard areas is especially striking. The branches and upper part of the stem are also exposed to decay organisms, analogous to preserved wood in above-ground applications. There are even trees, such as the mangrove species, that grow in a marine environment and face the same teredos, limnoria, etc. that wooden pilings used in docks and piers are exposed to.

There is one area of comparison, however, where the similarities break-down. We are quite happy if treated wood lasts 50 years in contact with the soil. This would not be acceptable to most tree species. Fifty years would be a minimum lifetime for most species and many grow much older. Coastal redwoods can be as much as 3,500 years old (1). Many tree species are much more successful at long-term wood preservation than we are.

If we can understand the mechanisms by which trees protect themselves from wood-destroying organisms, perhaps we can adapt them for our own use. In this paper, the protection mechanisms of trees against fungi and other pathogens will be discussed and compared to conventional wood preservative technology. Some of the literature and research done at MTU on using natural products as wood preservatives and surveying naturally decay resistant wood species for preservative chemicals will also be discussed.

DEFENCE MECHANISMS OF TREES

Trees can have two basic types of defence mechanisms - active and passive. Active responses only occur in tissues having living cells and are the result of some type of stimulus, such as mechanical wounding or formation of a decay pocket due to the action of invading organisms. The end result of the active response is to compartmentalize the site of infection from the remainder of the tree through chemical and physical barriers. These barriers are not present before the response occurs. In the passive defence systems, the components of the defence mechanism are always in place. Examples of this are the toxic extractives present in the heartwood of many tree species, and the bark, which often contains a plastic-like material (suberin) that is a physical barrier to attack by pathogens. This type of mechanism is analogous to commercial wood preservation methods.

Compartmentalization and Phytoalexins

Most infections found on tree stems are initiated by a mechanical wound caused by animals, weather, etc. that subsequently becomes colonized with a succession of infecting organisms. The primary response of the tree is to create barriers around the infection site to prevent its spread (2-4). These barriers can be

of a chemical nature through the accumulation of toxic compounds in the tissues surrounding the site, or physical by the blocking of open cells in the tissues in the areas around the site and the formation of regions with a high suberin content. Suberin is a complex polyester, normally found in quite large quantities in the bark of trees, that few organisms have enzymes capable of digesting (5,6). Since the infection cannot get through the suberin layer, it is prevented from spreading in that direction.

The toxic chemicals that accumulate around the site of infection to restrict its spread are called phytoalexins. This is a general term for any relatively small, biocidal compounds produced in response to attack by a pathogen. The phytoalexin response is found in many plant species (7-9), but has been most extensively investigated in annual crop plants. There is also growing interest, however, in this defence mechanism as it occurs in trees (10-12). Some chemical structures of tree phytoalexins are shown in Figure 1. The phytoalexin response is easily seen in black locust wood (Robinia pseudoacacia) because of the flourescence of one of the sapwood phytoalexins, robinetin (3,7,3',4',5'-pentahydroxyflavonol). In a stem cross-section from a fungal infected tree, the bright yellow flourescence of the robinetin around sites of fungal infection in the sapwood is readily seen.

The phytoalexin mechanism is potentially a rich source of natural products that could act as models for commercial wood preservatives. The biocide screening programs on tree species that have taken place in the past have only examined the extractives normally present in the tree, since the phytoalexins are only found in a damaged plant, they would not have been included in these studies. During the evolution of the phytoalexin system in a tree, it would be expected that the more effective phytoalexins will be selected for, as this will help maximize a plant's reproductive potential. There are likely to be many chemicals used by trees as phytoalexins that are effective pesticides. Identifying and evaluating phytoalexins for wood preservative application may result in new leads for wood preservative chemicals.

Wood Extractives

The natural wood decay defence most closely analogous to commercial treatments is the presence of toxic extractives in the heartwood of many tree species (14-16). There has been considerable interest in identifying wood extractives that have antifungal, insecticidal, and anti-borer activity. The program of the U.S. Navy

has been particularly comprehensive (15-21). Woods having natural resistance to wood-destroying organisms were identified through marine and terrestrial field tests, and the active extractives in the most resistant woods identified. This work resulted in the identification of several compounds that could form the basis for new types of preservative agents (22), especially a marine borer deterrent, obtusaquinone (structure I). Other important classes of protective wood extractives are the tropolones, stilbenes, and condensed tannins. Representative members of these chemicals are gamma-thujaplicin (structure II), astringenin (structure III), and a procyanidin (structure IV), respectively.

In North America, the most familiar naturally durable species are those from which commercial timber is cut - western red cedar, redwood and, to some extent, bald cypress. The active extractives of western red cedar have been the most extensively investigated (24), probably because of the relatively simple chemistry of this species. The most abundant extractive, gamma-thujaplicin (I), has a structure based on the seven-membered tropolone ring and is a good fungicide with an activity comparable to pentachlorophenol (23). The copper complex of beta-thujaplicin has an activity 70 to 100 times higher, at least against yeast (24). Thujaplicins are found in the heartwoods of many of the durable tree species of the Cupressaceae family. Tropolones are also synthesized by other organisms such as bacteria, which produce it as an antibiotic (25,26). Patents have been taken out on the production of tropolones by fermentation with some of these bacterial species (27,28). Commercial production of tropolones by extraction of heartwood from cedar species has also been proposed (29,30).

It is commonly observed that a durable wood can be exhaustively extracted with solvents, yet still remain relatively decay resistant (31). Furthermore, if a nondurable wood sample is then treated with the extract, it will often not have the decay resistance of the original decay-resistant wood. There are many factors still not understood about what makes a wood naturally durable.

One way these observations could be explained is through covalent bonding between some extractives and the polymeric wood cell components, cellulose, hemicellulose, or lignin. If the cellulose is derivatized in this way, it could make the wood decay-resistant in a similar manner to wood modified by acetylation (32). To explore the hypothesis that covalently bound flavonoids

contribute to the decay-resistance of condensed tannin-containing species such as redwood (1), we exposed wafers of southern pine sapwood to condensed tannins using a proprietary method that would promote the formation of bonds between tannin residues and wood cell wall components.

Some results from these experiments are summarized in Table 1. The weight loss of wafers reacted with condensed tannins (extracted from red or southern pine bark) after exposure to Gloeophyllum trabeum was only 1%, not significantly different from zero. The weight gain due to the treatment was 2%. Both figures were determined after extensive leaching of the wafers. Control wafers exposed to the same derivatization conditions, but without tannin present, lost 24% due to decay. Wafers were also simply pressure-treated with condensed tannin solution. These samples were less decay-resistant even after treatment with very high concentration tannin solutions that resulted in the same 2% weight gain in the wood after leaching. In other work, we also found that wood derivitized with condensed tannins is also more dimensionally stable than unreacted southern pine samples. Both dimensional stability and decay resistance are characteristics of naturally durable species. With this tannin derivitization procedure it appears to be possible to make a semi-synthetic analogue of redwood using southern pine and bark extracts as the raw materials.

Tree Barks

Bark is normally the first tissue that a pathogen such as a fungus or insect encounters on the stem, roots or branches of a tree. It is logical that the plant will have evolved particularly effective defences here. This need for defence is especially clear for tree roots. In most tropical or sub-tropical environments, unprotected wood on the forest floor is quickly decomposed by fungi and termites. Roots and the lower part of the tree's stem are exposed to these same hazardous conditions, yet survive very well. In some work on black locust, we have found that the stem and root barks are quite different. There are phenolic extractives in the root bark, not present in the bark from the trunk, that may be involved in resistance to decay organisms. However, the defensive mechanisms in the stem and root barks are not well understood. There is very little information in the literature on the functional chemistry of barks, probably because of the chemical and anatomical complexity of these tissues compared to wood. The root bark of tropical trees, however, has become a favorite source of new chemicals for drug screening programs because of this chemical complexity. Although there has been little effort spent on why plants have these biologically active compounds localized in their roots. It is clear that tree barks are probably good materials to examine for chemicals with wood preservative efficacy.

There are two classes of natural products commonly associated with tree barks, condensed tannins (described above as also a wood extractive) and suberin. Condensed tannins (e.g. IV, a procyanidin) are hydroxylated aromatic polymers based on the 15-carbon flavan monomer. They are widespread phytochemicals, being found in the fruit, fruit pods, seeds, seed shells, foliage, wood and/or bark of a wide variety of species (33,34). The structure and chemistry of the condensed tannins have only been begun to be understood recently (35-40). The average molecular weight or degree of polymerisation of condensed tannins can vary considerably with the source, with important effects to the properties of the polymer, especially the solubility. High molecular weight tannins, commonly found in tree barks, are not soluble in neutral solvents (40). This makes the determination of tannin content difficult. In some species, however, it appears that over 50% of the bark's dry weight can be condensed tannins (41).

Tannins exert their pesticidal effects through their ability to complex with proteins. Most wood-destroying fungi grow by excreting extra-cellular enzymes that break down the wood constituents so they can be absorbed and metabolised by the fungus. If condensed tannins are present, they form a complex with the enzyme, rendering the latter insoluble and inactive. The same chemical functionality that allows this protein complexation, the ortho 3,4-dihydroxy aromatic ring of the monomers, is also capable of complexing with metals. This ability allows condensed tannins to behave as a fixative for copper in wood preservative systems.

Copper(II) salts and complexes are effective and environmentally safe fungicides. This metal forms the basis for the preservative efficacy of CCA, copper naphthenates and copper quinolinolate, as well as other fungicidal systems. We have investigated the use of condensed tannins complexed with copper ions as wood preservatives for both ground-contact and above-ground applications. A representation of the type of complex that could form between a procyanidin, the type of condensed tannin found in southern pine bark, and copper(II) is shown as structure V.

Laboratory testing has shown that tannin/copper(II) complexes are effective wood preservatives (Table 2, references 42,43). Condensed tannin-containing bark extracts from loblolly pine (Pinus taeda) were evaluated using ASTM soil block methodology (D1413-81) in both complexed and uncomplexed forms. Bark extracts by themselves did not cause any reduction in weight loss of pressure-treated wood blocks at the retentions tested. They do have efficacy, however, as wood preservatives when complexed with copper (II) ions. The best experimental wood preservative formulation shown in Table 2 is a dual treatment entailing initial impregnation with an aqueous sulphited southern pine bark extract, followed by treatment with an aqueous solution of $CuCl_2$. At some retentions, this method yielded wood blocks with greater resistance to decay by Coriolus versicolor, a standard white-rot fungus, than pentachlorophenol. At a total retention of 10 kg/m^3, wood samples

treated with the sulphited tannin extract/$CuCl_2$ combination had about one third of the weight loss of pentachlorophenol at approximately the same loading.

The commercial preservative system probably most similar to a copper/polyflavonoid system is copper naphthenate. Both rely on copper to be the primary fungicidal component, while the naphthenic acid and polyflavonoid components are mainly there to provide fixation sites for the copper, along with some supplementary antifungal activity. In a soil-block comparison of a sulfited spruce extract/copper system with ammoniacal copper naphthenate, the tannin-based system was more effective (Table 3).

For commercial applications, a treatment method where the tannin-containing extract and copper salt could be applied in one step would be very desirable. Simply combining the two components in water results in formation of an insoluble complex. An aqueous ammonia solvent, however, will dissolve the complex. Unfortunately, exposing the extract to the alkaline conditions of the ammonia solution reduces its preservative efficacy. Wood blocks treated with the ammoniacal complex have a greater weight loss than samples exposed to the dual treatment (Table 2). This is probably due to alkaline rearrangements occurring in the tannin during the treating process that reduces its preservative efficacy (44). We have subsequently found that the polyflavonoid/copper complex is soluble in water-ethanol combinations and are currently evaluating the efficacy of this type of treating solution, as well as oil-borne formulations.

Work has also been done by Lotz and Schmidt (45,46) on using imported commercially-available condensed tannins from wattle and quebracho trees as wood preservatives. It was reported that these tannins can be fixed into wood by using non-ionic surfactants in a second treatment step to give wood blocks resistance to decay. This type of fixation could be valuable in developing an above-ground treatment based only on condensed tannins.

The other widely occuring, characteristic component of tree barks is suberin. This is a natural polyester composed of hydroxy and epoxyhydroxy fatty acids, along with some aromatic carboxylic acids. Some of the major monomers in birch bark are shown in Figure 2. Suberin is found in many plant barrier tissues besides bark, and is associated with healed or healing wounds. The outer bark of birch tree is especially rich in this polymer, making up about one third of its dry weight (47). Suberin is an important constituent of plant protective tissues because it is relatively difficult for pathogenic organisms to degrade it (48). This is clearly seen in birch forests where the bark will persist long after the wood within a stem has been completely decomposed.

A wood preservation technique analogous to birch bark is the use of plastic coatings of various types by the Port of Los Angeles to protect marine pilings. Even after 25 years, these plastic

coatings are still performing well as a wood protectant system. Mangrove tree species have evolved along seashores with constant exposure to the same hazards that marine pilings are exposed to. Although the suberin content of mangrove bark has not been reported, it is interesting that this bark is very high in condensed tannin content (49,50). In fact, at one time mangrove bark was a commercial source of tannins for leather manufacture. The high tannin content in mangrove barks indicates that wood preservatives based on condensed tannins may also have efficacy in marine applications.

The use of natural products for wood preservatives, or as models to develop synthetic pesticides for this use, may seem quite esoteric to many workers in this field. However, this is a well-accepted approach in the search for compounds with biological activity. A number of commercial insecticides are, or are based on, natural products. Good examples of this are rotenone and the pyrethroids. There is currently great interest, both commercial and academic, on a tree which produces compounds with potent insect antifeedant properties (the neem tree, Azadirachta indica). Of course, natural products are used in many pharmaceutical applications, as well. Some of the most potent antifungal compounds known are produced by other fungi. The evaluation of trees for compounds with antifungal and antitermitic properties may lead to a new approach for wood preservation. It is appropriate that aspects of one of man's most recent sciences, biotechnology, be used to solve one of his oldest problems, wood preservation.

CONCLUSION

A need for new more socially acceptable wood preservatives has developed out of pressure from the EPA and consumer's groups. A potentially important source of new wood preservative chemicals and systems is from trees, themselves. Over the many millions of years of plant evolution, trees have evolved very sophisticated mechanisms to protect themselves from the predations of fungi and insects. These mechanisms can be very effective, giving individuals of some tree species lifetimes measured in the thousands of years. In contrast, the ability of commercial preservation techniques to protect wood is much less effective. Many of these natural defence mechanisms of trees, however, are poorly understood.

In laboratory evaluations, we have found that wood preservative formulations based on condensed tannins, a major component of many tree barks, can have good efficacy. The advantages of a formulation based on tannins are many. Since tannins are a significant component of our diet, it would be expected that a wood preservative based on them would have a reduced impact on the environment during manufacture and treatment, and also be safer for the users of the treated wood, than conventional treatments. The consumer appeal of a wood preservative system based on natural products could also be important. Condensed tannin wood preservatives would also be based on a renewable resource, avoiding all the economic and social problems associated with petrochemicals.

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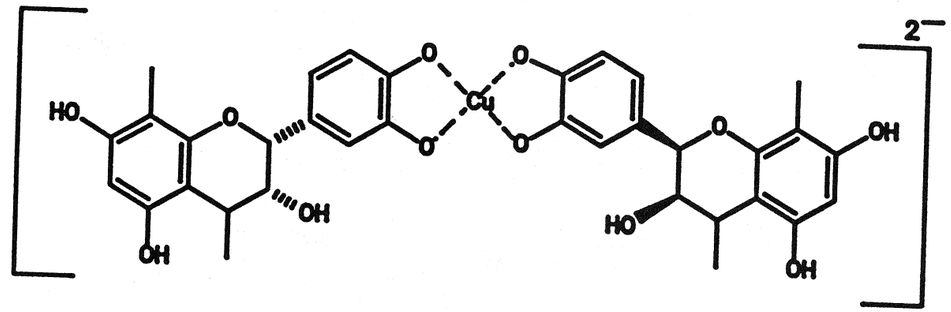
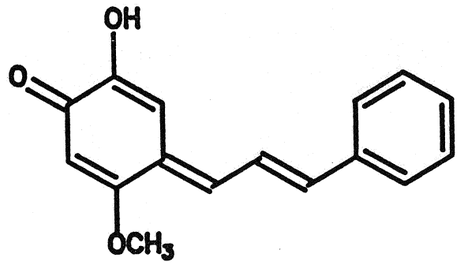
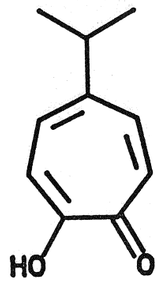


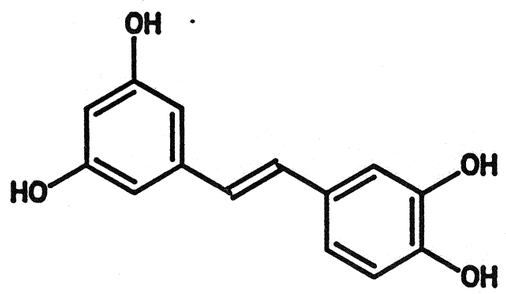
V - Tannin/Copper Complex



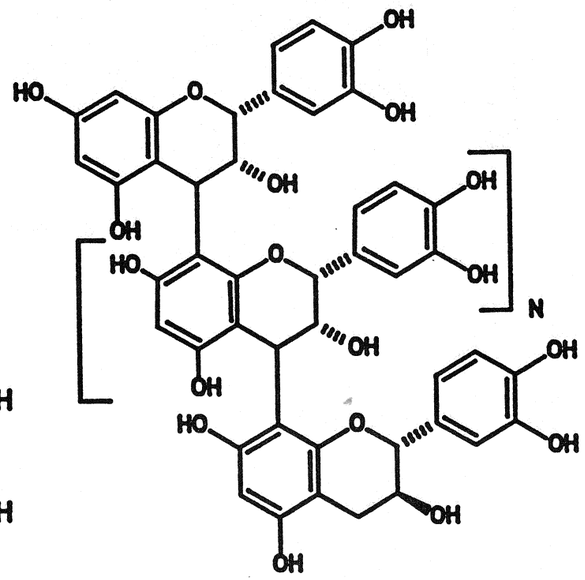
I - Obtusaquinone



II - Gamma-Thujaplicin

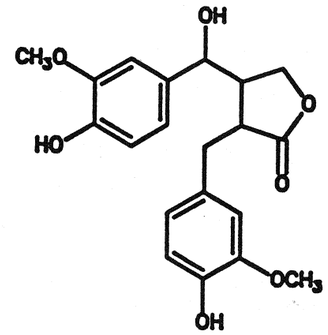


III - Astringenin

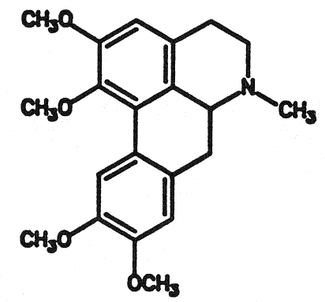


IV - A Procyanidin

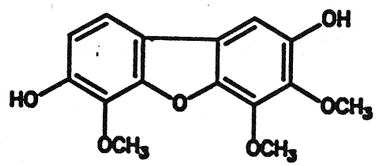
Figure 1. Some phytoalexins from tree species.



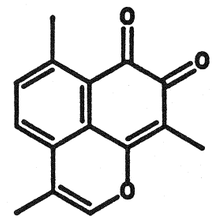
Hydroxymatairesinol
Picea abies



Glaucine
Lirodendron tulipifera



Cotonefuran
Cotoneaster lactea



Mansonone F
Ulmus hollandica

Figure 2. The major suberin monomers in white birch bark.

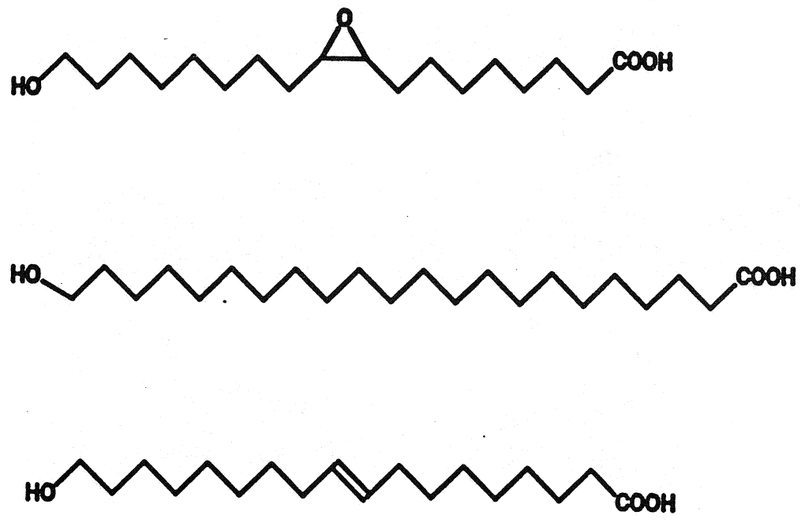


Table 1. Decay resistance of condensed-tannin modified southern pine wafers and controls, after leaching, to Gloeophyllum trabeum. In the non-reaction treatment, the wafers were simply pressure treated with a condensed tannin solution.

Treatment	Retention	Weight Loss
Derivitization Reaction	2 %	-1 %
Solvent Control	-1	-24
Non-Reaction Treatment	2	-9

Table 3. Results from soil block (birch) tests (ASTM D1413-81) comparing copper-complexed, black spruce bark sulfited extract (dual treatment) to ammoniacal copper naphthenate, after exposure to Coriolus versicolor.

Treatment	Retention (Kg/m^3)	Average Weight Loss (%)[1]
Extract + $CuCl_2$	2.96 + 1.46	7.3
	5.93 + 2.91	2.7
	12.13 + 5.91	0.0
	22.25 + 11.32	0.0
Extract	2.05	51.8
	4.42	55.5
	8.56	50.3
	17.45	48.4
Ammoniacal Copper Naphthenate	3.06	39.4
	5.99	11.9
	12.07	4.0
	24.24	0.0
Untreated Controls	---	>50.0

[1]Average of five replicates.

Table 2. Soil block tests using copper-complexed, loblolly pine bark sulfite extract (LPBSE) and loblolly pine bark acetone/water extract (LPBAWE) treated with a two stage procedure and LPBSE/$CuSO_4$ in aqueous ammonia, compared to pentachlorophenol, $CuCl_2$ and untreated controls with the white rot fungus C. versicolor.

Treatment	Conc. in Soln. (%)		Mean Retention[1]		Mean % Wt. Loss (S.D.)[1]	
	Organic Component	Copper Salt	Organic Component	Copper Salt		
LPBSE II + $CuCl_2$	0.5	0.25	3.09	1.53	15.3	(3.8)
	1.0	0.5	6.26	3.14	2.6	(1.2)
	2.0	1.0	12.34	6.27	1.5	(1.2)
	4.0	2.0	22.93	12.22	0.3	(0.4)
LPBAWE + $CuCl_2$	0.5	0.25	3.53	1.77	49.0	(10.2)
	1.0	0.5	7.13	3.58	32.7	(9.0)
	2.0	1.0	14.23	7.07	18.5	(3.8)
	4.0	2.0	29.38	13.75	11.5	(2.2)
1:1 LPBSE/$CuSO_4$ in 10% NH4OH	1.0		6.09		32.1	(6.2)
	2.0		12.47		13.6	(2.5)
	3.0		18.60		8.1	(2.1)
	4.0		24.87		3.1	(0.8)
	5.0		31.46		1.0	(0.6)
Pentachlorophenol (Ethanol Solvent)	0.5		2.52		62.3	(6.9)
	1.0		5.05		33.6	(4.0)
	2.0		10.27		7.0	(1.8)
	3.0		15.19		0.9	(1.5)
$CuCl_2$ Only	0.25			1.49	35.3	(6.7)
	0.5			2.97	15.5	(5.9)
	1.0			6.11	11.4	(1.8)
	2.0			12.18	12.1	(3.3)
Untreated Controls	---		---		>50[2]	

[1]Average of 5 replicates.

[2]Blocks in these sets could not be separated from the soil.