

A Preliminary Investigation of the Marine Borer Resistance of the Tropical Wood *Dalbergia Retusa*

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ABSTRACT

The wood of the tropical tree *Dalbergia retusa* (Cocobolo) was the most resistant to marine boring organisms of 113 species tested in an 8-year tropical exposure study. The first step toward identifying the constituent(s) affording such high resistance has been taken. Panels of *Dalbergia retusa* were extracted with one of three solvents—ethanol, acetone, or toluene—and exposed to marine borer activity in Panamanian waters. All of the alcohol- and acetone-extracted panels were severely damaged by borers; the toluene-extracted panels were much less damaged. None of the extracts was able to confer protection to highly susceptible Southern yellow pine, possibly because of heat inactivation of the protective component, an insufficient quantity of this material deposited in the pine, or both. Some of the control panels, which were fabricated from a proven highly resistant supply of *D. retusa* were damaged by borers. Air oxidation of the protective factor in the outermost layer of wood cells may have been the causative factor. A more comprehensive chemical fractionation of *D. retusa* is underway. All of the fractions are being assayed for antiborer activity using the larvae of the teredinid *Lyrodus pedicellatus* and for fungal activity against certain lignin- and cellulose-destroying marine fungi. Those fractions proving active will be further fractionated and assayed again. Methods for using the most potent fractions, or components thereof, to treat coniferous marine construction timbers will be studied.

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This is an interim report; work on this project is continuing.

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A PRELIMINARY INVESTIGATION OF THE MARINE BORER RESISTANCE OF THE TROPICAL WOOD *DALBERGIA RETUSA*

INTRODUCTION

As man extends his activities into the sea, a knowledge of the biological, chemical, and physical effects of the marine environment on the materials of his equipment and structures becomes increasingly important. Of all the structural materials available today to the marine engineer, wood has the longest history of use and continues to enjoy a position of importance because of its many unique properties and relatively low cost. Although the durability of wood in the marine environment is high in the absence of marine boring organisms, when these animals are present wooden structures become infested and severely damaged. It is difficult to assess accurately the cost of such damage in terms of replacement or repair of marine structures because often cost accounting procedures fail to delineate expenditure in this category from the total expenditure for replacement and repair. It has been estimated, however, that in the United States the annual bill for this damage may average 200 to 250 million dollars (1). The Navy shares a large portion of this cost.

One of the most frequently used and most successful of the current methods of borer protection for wood is pressure treatment with whole creosote; however, in tropical and subtropical waters creosoted timbers are often destroyed in a few years. Other chemical preservative treatments also have less than satisfactory service records, often providing virtually no protection to the wood. Besides these variable and frequently unsatisfactory results obtained with chemical preservatives, they pose another problem which manifests itself in the recent upsurge of public interest in environmental pollution. As this interest continues to increase, the use of chemicals as protective agents becomes increasingly suspect. The field of wood preservation is not immune to this trend because all of the standard wood-treating techniques, both for terrestrial and marine use, are toxic chemicals. It is conceivable that many of these chemicals will become unacceptable in the future as wood protectants because of their potentially adverse impact on the environment. Consequently, the importance of developing nonpolluting methods to control organisms detrimental to man's goods takes on a new urgency.

An alternative approach to wood protection by chemical means is to seek out wood species having natural resistance to those organisms causing damage. These species could then be used as nonpolluting substitutes for susceptible timbers that must be heavily treated with potent synthetic chemicals or chemical mixtures, such as creosote or chromated copper arsenate. A limited number of woods are reputed to have a high natural resistance to certain boring organisms in the marine environment. Ordinarily these woods have a very local reputation and only a few, such as *Ocotea rodiei* (Greenheart) and *Dicorynia paraensis* (Angelique) have been marketed worldwide on this basis. While the latter woods have been very successful in some installations, success has not been universal, particularly in tropical regions. Very few studies have been made on the natural resistance of woods in the marine environment. Notably among these is the work of

Edmundson (2) and of the Clapp Laboratories (3). In a more recent search for naturally resistant woods, NRL collected and exposed 113 species to borer attack (4). Of this group 104 species were indigenous to the tropical forests of Panama and 9 species were reputedly borer-resistant woods gathered from other tropical regions of the world. The woods were exposed for periods up to 90 months in three different tropical waters—the Caribbean Sea at Coco Solo, C.Z., the Pacific Ocean at Naos Island, C.Z., and the brackish Miraflores Lake, a section of the Panama Canal, and all were evaluated separately for teredo, limnoria, and pholad damage.

The species most resistant to all marine borers was *Dalbergia retusa* (Cocobolo). No correlation could be made between the exceptionally high borer resistance of this species and the silica content of the wood, which was found to be only 0.004% (4). It possesses an oily constituent, which is known to cause dermatitis in some people; its borer resistance may also be related to this substance. Although the generally small size and irregular shape of this tree make it unsuitable as a source of marine construction timbers, the species is of special interest because of the possibility of isolating and identifying the component conferring borer protection to the wood and using this material to treat less resistant conventional marine construction timbers. The purpose of this investigation is to determine the nature of this protective constituent, and some preliminary results are presented in this report.

BACKGROUND ON *DALBERGIA RETUSA*

Dalbergia retusa Hemsl. is a Central American member of a pantropically distributed genus of the family Leguminosae containing about 250 species of trees and scandent shrubs. It was first described by Hemsley in 1878 (5) and, along with *D. hypoleuca* Pittier of Costa Rica and *D. granadillo* Pittier of Mexico, produces the economically important tropical hardwood Cocobolo, which was introduced into commerce from Panama in the late 19th century. These three species are quite similar and, according to Record and Hess (6) in terms of structure and properties of the timber, all the Cocobolo of Central America can be considered to be *D. retusa* or at least varieties thereof. The combined range of these species extends from southwestern Mexico to the Darien Province of Panama, and possibly into northwestern Colombia. It is reported, however, that *D. retusa* is the only *Dalbergia* of tree size to be found in Panama (7,8), where it grows, infrequently, as lone trees or in small groves in the understory of the mixed tropical hardwood forests in the drier upland regions of its range.

A botanical description of the herbarium or an anatomical description of the wood will not be presented here, although a few descriptive comments are in order. Physically, *D. retusa* is often poorly formed as a consequence of its growth environment (7), although it may attain a height of 75 ft and a diameter of about 16 in. The heartwood which has proven so resistant to degradation by marine boring organisms may constitute only half of the diameter of a tree, the rest consisting of the off-white or pale yellow sapwood which is reported to have no durability or commercial value. As the tree ages, the thickness of the sapwood band decreases until in large, old trees, it may only extend an inch or so into the trunk (6). The demarcation between sapwood and heartwood is very sharp, as shown in Fig. 1; the reddish-colored heartwood has an oily appearance and feel. Both the heartwood and sapwood are quite hard and heavy and have a density greater than one, and a moisture content of about 5%.



Fig. 1—Stump of a newly harvested tree of *Dalbergia retusa* showing the relative proportion of sapwood and heartwood and the striking color change and sharp boundary existing between them

EXPERIMENTAL DATA

Panel Preparation and Extraction

The 1/4-by-1-1/2-by-3-in. panels, which were fabricated from the same supply of *D. retusa* that had served as a source of specimens in the original exposure of this wood (4), were dried to constant weight at 105° C. The panels were then divided into three groups, and each group exhaustively extracted in a Soxhlet apparatus with one of three solvents—ethyl alcohol, acetone, or toluene. The extractions were terminated when a sample withdrawn from the extraction chamber left no appreciable residue on evaporation to dryness. After extraction the panels were again dried to constant weight to free the wood of residual solvent and to determine the amount of material that had been removed. Weight-loss data for the extracted panels are presented in Table 1.

Panel Impregnation

A combined extract (from panels and wood chips) for each of the solvent systems was concentrated and used to impregnate highly borer-susceptible Southern yellow pine panels by a modified Bethel full-cell treatment (9). The panels were subjected to a vacuum of about 10 mm Hg for 60 minutes before the extract was allowed to enter the evacuated working chamber of the impregnating device. After venting the chamber to atmospheric pressure, the contents were subjected to 100 psi nitrogen for an additional 60 minutes. When the pressure was released, the panels remained submerged in the extract for 15 minutes to allow pressure equilibration with the interior of the wood. Upon removal from the chamber, the panels were immediately wiped free of excess solution

Table 1
Average Weight Loss for Each Group of *D. retusa* Panels at Various Stages of Their Processing

Solvent	Panel No.	Original Wt.	Dried Weight Before Extraction	Dried Weight After Extraction	Material Lost On Extraction	Dried Weight After Exposure	Material Lost During Exposure
Ethanol	1-10	21.80 ± 0.82	20.68 ± 0.99	17.39 ± 0.43	3.29 ± 0.74	11.34 ± 1.62	6.05 ± 1.62
Acetone	11-20	21.47 ± 1.01	20.20 ± 1.00	17.60 ± 0.89	2.60 ± 0.61	12.43 ± 3.02	5.17 ± 2.68
Toluene	21-30	21.64 ± 1.51	20.46 ± 1.09	20.15 ± 1.08	0.31 ± 0.17	17.23 ± 3.44	2.92 ± 2.55
Controls	31-40	22.09 ± 0.89	21.00 ± 0.69	—	—	19.72 ± 3.81	1.28 ± 1.22



Fig. 2—An exposure array of extracted *Dalbergia retusa*

and weighed; the increase in weight was converted to a volume equivalent of solution, assuming the density of the extract to be that of the pure solvent. From this calculated volume and the solids concentration of each of the concentrated extracts, the concentration of material deposited in the pine could be determined. The solid content of the extracts was determined by evaporating an aliquot of each extract to dryness at room temperature in a stream of dried, filtered air.

Exposure Procedure

Half of the extracted panels obtained from each solvent system and half of each set of impregnated panels were randomly mounted along with suitable controls on a rigid polyvinyl chloride pipe (Fig. 2) and exposed in the Bay of Panama. The exposure site, 1-1/2 miles from the natural shore line, is located at the Smithsonian biological collection pier adjacent to the Ft. Amador causeway at Naos Island, C.Z. The remaining panels of each set were similarly randomized and the specimens placed on exposure in Manzanillo Bay, an arm of the Caribbean, at Coco Solo, C.Z.

After 6 months in the marine environments, the panels were removed, air-dried, and returned to the laboratory where they were cleaned of their fouling cover, dried to constant weight, and the extracted panels x-rayed to reveal the extent of internal damage. When part of a panel was missing, a proportional weight adjustment was made based on the assumption that the intact panel had been uniformly damaged.

The impregnated pine panels were so heavily damaged that x-ray photography was not required.

RESULTS AND DISCUSSION

The extent of damage sustained by the extracted *D. retusa* panels is shown in Fig. 3 for those panels exposed at Naos Island and in Fig. 4 for those panels exposed at Coco Solo. It is obvious from these x-ray photographs that the latter panels were more heavily attacked than those panels exposed in the Pacific Ocean at Naos Island; these results reconfirm the continuing existence of a high level of borer attack in Caribbean waters. It is also obvious that both the alcohol and the acetone were very effective, and nearly equally so, in removing a protective substance from the wood. When the average weight loss for each set of extracted panels (Naos Island and Coco Solo combined) was compared by Student's "t" with that of the controls, the differences between these pairs of values were highly significant with a probability of less than 0.001 that they could have arisen by chance. Although some of the toluene-extracted panels were damaged, this solvent was not as effective in removing an active component from the wood. Unlike the other two groups of panels, the damage sustained by this group varied from none to heavy. Again by Student's "t" the average weight loss of the toluene-extracted panels did not vary significantly from that of the controls (probability = 0.1), thereby, substantiating the null hypothesis that no difference existed between the two sets of data and that the toluene was not effective in removing an active substance from the wood. This selective solubility of the active material suggests that it might be a large molecule with multiple polarities.

Since a protective substance had been removed from *D. retusa* by alcohol or acetone extraction, these extracts might be expected to confer some degree of protection to very-borer-susceptible Southern yellow pine. However, none of the *Dalbergia* extracts were capable of protecting the impregnated panels as shown in Figs. 5 and 6 for Naos Island and Coco Solo, respectively, although those panels exposed at Naos Island were somewhat less damaged than those at Coco Solo. *Limnoria* activity, which was quite heavy at the latter site, contributed considerably to the excessive damage suffered by the panels exposed there. While it is still not definitely known why these extracts failed to protect the pine, information received subsequent to these exposures suggests that the active component may be heat sensitive and had been rendered inactive during the drying of the panels or by exposure to boiling solvents. Working in concert with heat sensitivity, the low level of impregnation in the pine achieved with the alcohol and acetone extracts may be another reason why these extracts were so ineffective in protecting the wood from borer damage. In both impregnations only about 1/3 of the solid material removed per unit volume of the extracted *Dalbergia* was successfully introduced into the tissues of the pine as shown in Table 2. Conversely, the concentration of the toluene-extracted material in the pine was more nearly the same as it was originally in the *Dalbergia*.

Failure of some of the control panels was quite unexpected. It is hard to understand why this wood which had been so resistant during the initial exposure should now become damaged in 6 months. Equally baffling is why only some of the controls were damaged while the others remained intact. Again, subsequent information indicates that some of the naturally occurring constituents of *D. retusa* may be sensitive to air oxidation over a prolonged period (10). The active material may be one of these substances. The wood from which the panels were cut was part of the original supply of this species obtained about 15 years ago. It is conceivable that the active material in those wood tissues adjacent to the surface could have been chemically altered over this period of time, and panels cut from this part of the wood did not contain sufficient protectant. It is important to try to determine the cause of this failure. As a preliminary effort, panels with differing surface histories are currently being exposed in the laboratory to the

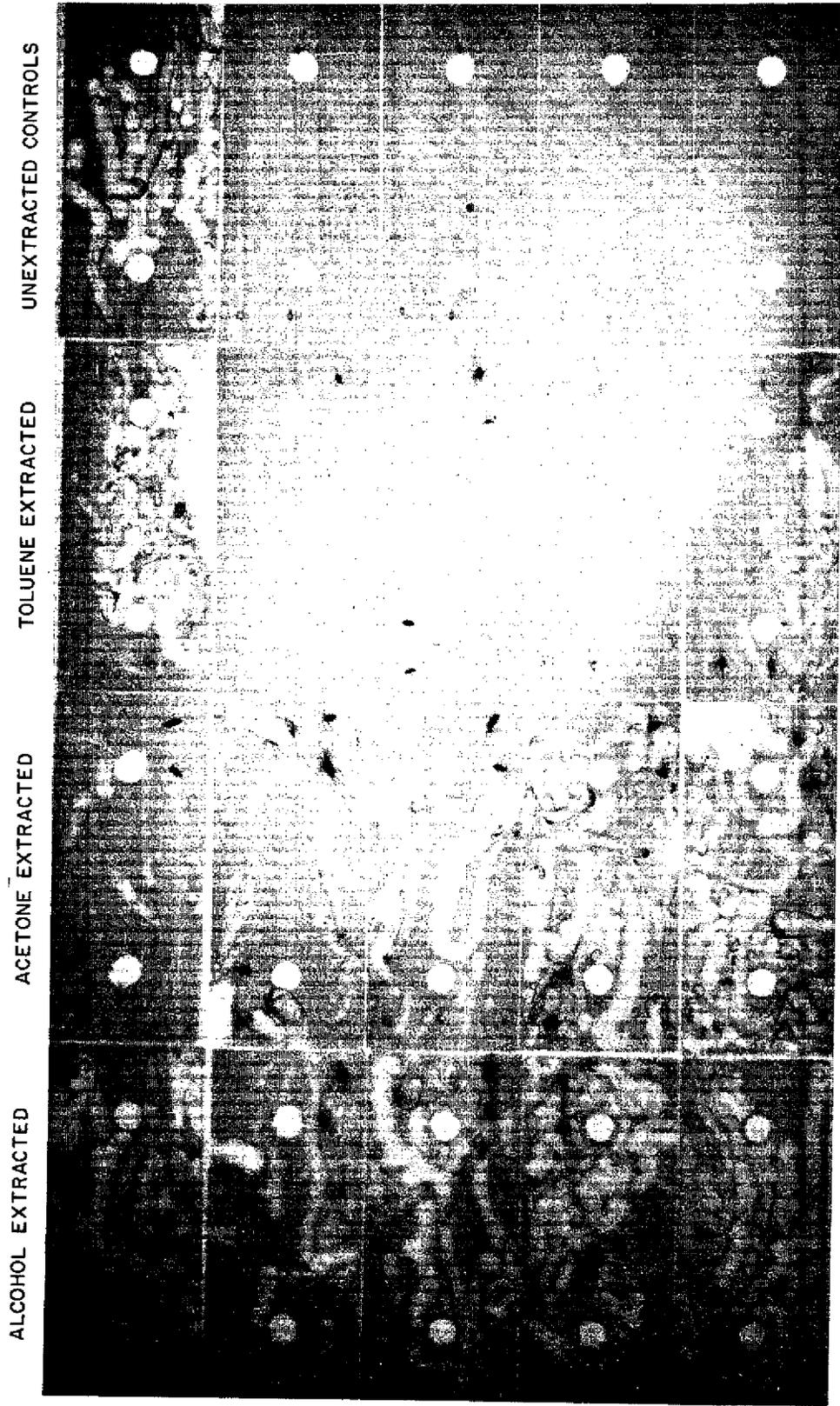


Fig. 3—X-ray photograph showing borer damage sustained by the extracted *D. retusa* panels exposed for 6 months at Naos Island, C.Z. The column headings indicate the solvent used to make the extraction.



Fig. 4—X-ray photograph showing borer damage sustained by the extracted *D. refusa* panels exposed for 6 months at Coco Solo, C.Z.
The column headings indicate the solvent used to make the extraction.

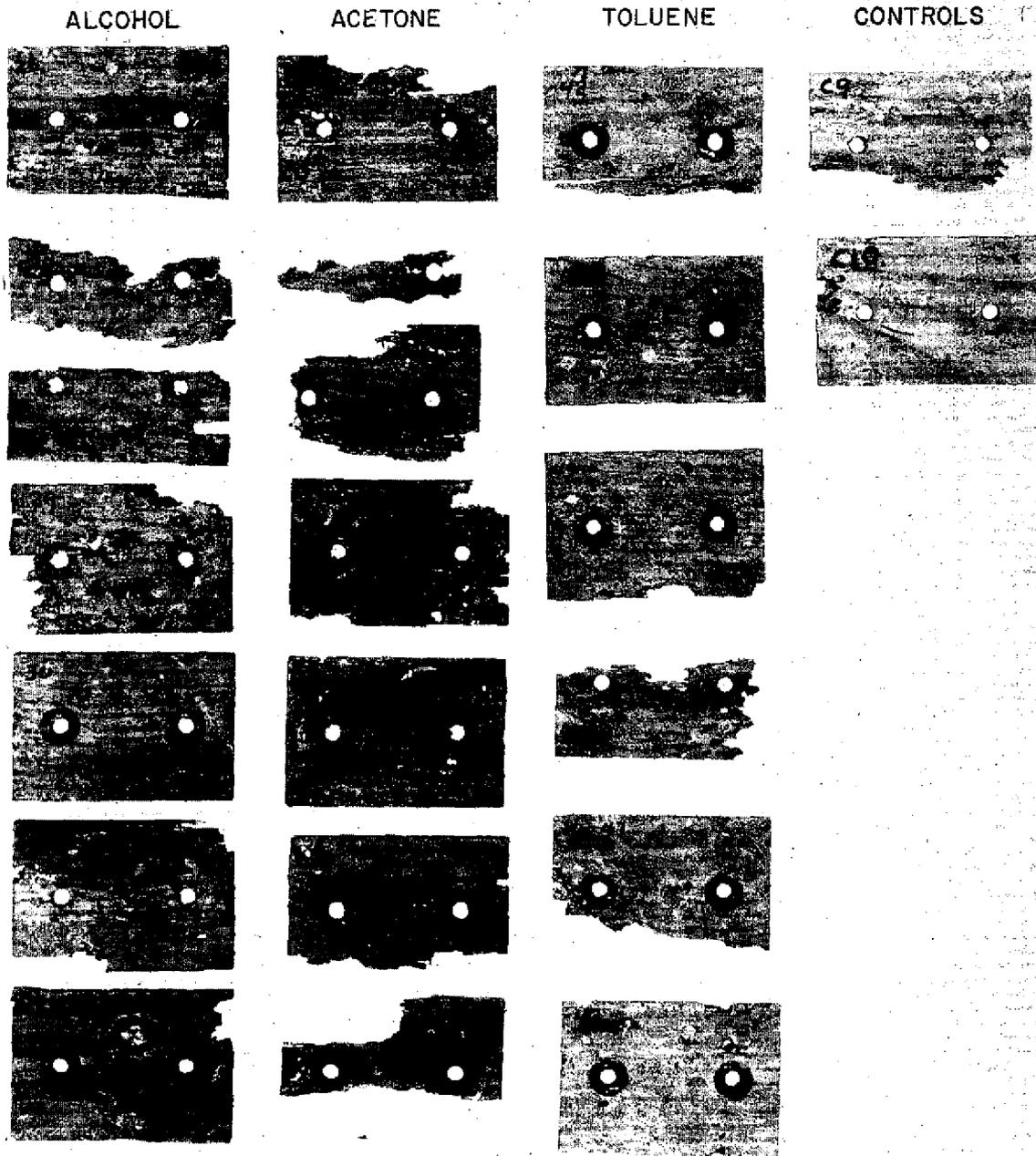


Fig. 5—Borer damage sustained by pine panels impregnated with the *D. retusa* extracts after 6 months of exposure at Naos Island, C.Z. The column headings indicate the extract used to make the impregnation.

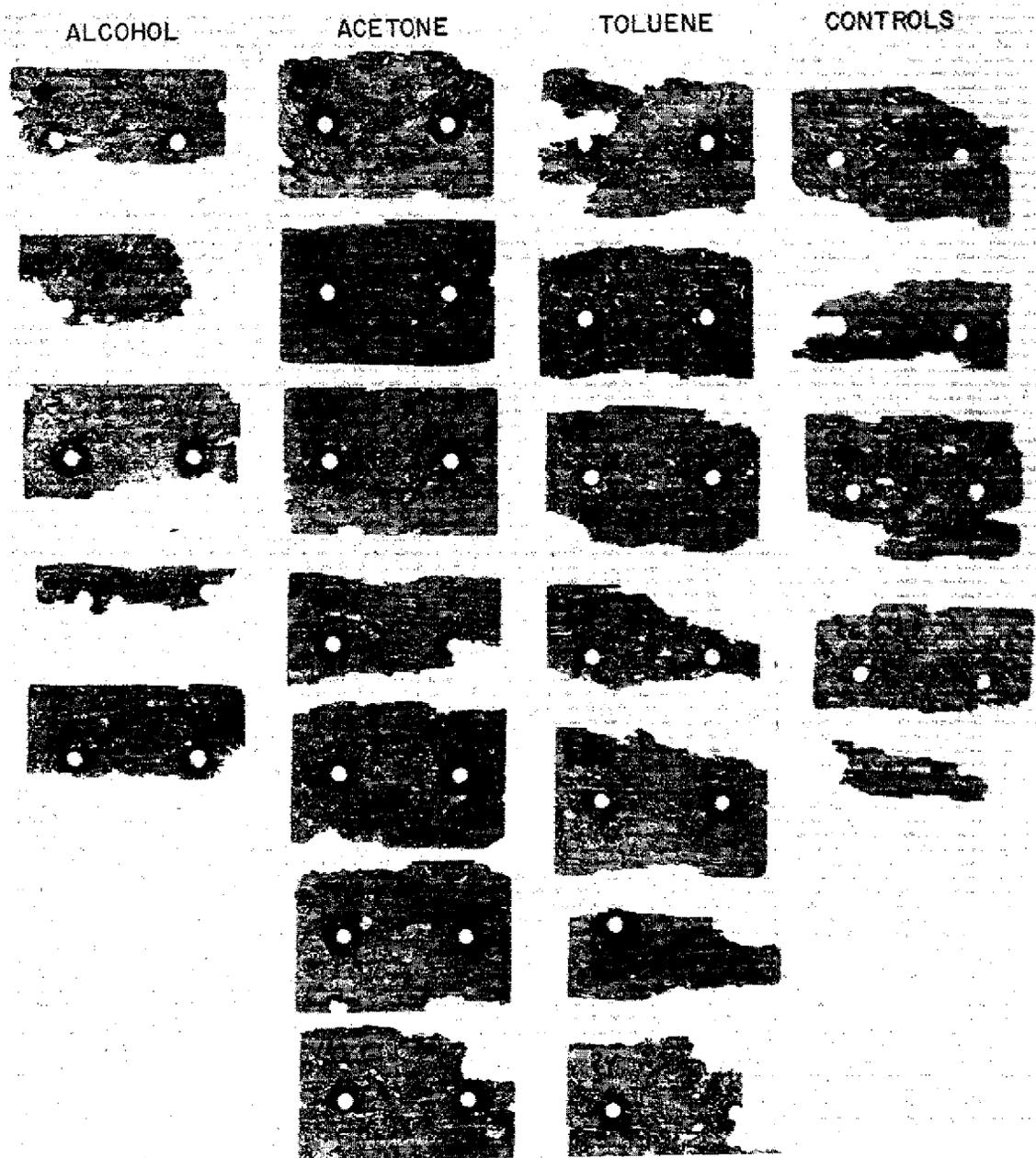


Fig. 6—Borer damage sustained by pine panels impregnated with the *D. retusa* extracts after 6 months of exposure at Coco Solo, C.Z. The column headings indicate the extract used to make the impregnation.

Table 2
Relative Concentration of the Extractable Materials in *D. retusa* and in the Pine

Solvent	Solid Concentration of Concentrated Extract (gm/cm ³)	Concentration of Extractables in <i>D. retusa</i> (gm/cm ³)	Concentration of Extractables in Pine (gm/cm ³)
Ethanol	0.083	0.18	0.060
Acetone	0.072	0.14	0.044
Toluene	0.019	0.017	0.011

larvae of *Lyrodus pedicellatus* to determine whether age of the surface is a factor in its resistance to successful attack by these organisms. Included in this exposure are an original wood surface exposed for 51 months in the Caribbean Sea at Coco Solo, C.Z., a surface generated when these stakes were sectioned for rating, and a newly generated surface. Results of this exposure are not yet available.

A fresh supply of undried *D. retusa* will be extracted with cold ethanol to eliminate any deleterious effect caused by heat on the active material. In addition, two improvements will be made to facilitate the pickup of extract solution by the wood; first, the pine will be impregnated with much more concentrated extract solutions than before, and, second, a technique of drying the wood by solvent replacement (11) will be used. This procedure will greatly reduce shrinkage of the structural units of the wood and leave the cell walls with a high degree of porosity. These changes should result in a much higher level of solids uptake per unit volume of wood, thereby, more nearly duplicating the natural concentration of these materials in *Dalbergia*.

A fresh supply of *D. retusa* is currently being extracted by classical extraction techniques employed in the isolation of natural products. Preliminary results indicate that the phytochemical composition of this species is going to be very similar to that of the other members of this genus. Each of the various solvent fractions will be assayed for bioactivity against the larvae of the teredinid *Lyrodus pedicellatus* and certain lignin- and cellulose-destroying marine fungi. Those fractions which are bioactive will be separated into their constituent components and each component assayed for activity. When the quantities available permit, white pine panels will be impregnated with the fractions and the individual constituents in addition to adding these materials directly to seawater containing a population of the larvae. The results of this study will be the subject of a later report.

SUMMARY

Each of three groups of *Dalbergia retusa* (Cocobolo) panels were exhaustively extracted with one of three solvent systems—ethyl alcohol, acetone, or toluene, and each of these extracts was used to impregnate highly marine borer-susceptible Southern yellow pine. All of the treated panels were subsequently exposed in the marine environments at Naos Island, C.Z., and at Coco Solo, C.Z., for 6 months.

All of the *Dalbergia* panels extracted with alcohol or acetone were severely damaged by marine boring organisms, while some of the toluene-extracted panels were either lightly damaged or not damaged at all.

None of the three extracts was able to confer protection to the vulnerable yellow pine. This failure may be attributed to the application of excessive or prolonged heat to the wood during the preparation of the panels which served to inactivate or destroy the active material, to an insufficient quantity of the protectant impregnated in the wood, or to both factors acting in concert.

Some of the *Dalbergia* control panels fabricated from the original supply of highly borer-resistant wood were also damaged by borers. It is hypothesized that during the 15 years since the wood was harvested the active material present in the peripheral layers of wood cells became inactivated by air oxidation and that the damaged control panels were cut from this portion of the wood.

A phytochemical investigation of *D. retusa* is underway. A preliminary fractionation of the wood indicates that many of the chemical constituents present in the tissues are related to those previously found in other *Dalbergia* species. Each of the various solvent fractions and constituents thereof will be assayed for bioactivity against the larvae of the marine borer *Lyrodus pedicellatus* and against certain lignin- and cellulose-destroying marine fungi.

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