

# THE JOURNAL OF AGRICULTURE OF THE UNIVERSITY OF PUERTO RICO

Issued quarterly by the Agricultural Experiment Station of the University of Puerto Rico, for the publication of articles by members of its personnel, or others, dealing with any of the more technical aspects of scientific agriculture in Puerto Rico or the Caribbean Area.

Vol. XXXIX

July 1955

No. 3

## Organic Termite Repellents Tested Against *Cryptotermes Brevis* Walker

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### INTRODUCTION

Escape to the Tropics, to avoid the high cost of living and the complexities of modern civilization, is a mirage which becomes most apparent as lengthy residence indicates compensating disadvantages. Insidious termite attack on furniture and the interior of wooden houses in the Tropics possibly cancels out any saving from unneeded heavy clothing and other means of protection from wintry blasts and snow and ice. The West Indian dry-wood termite, *Cryptotermes brevis* Walker, is as omnipresent a symbiot of man in Puerto Rico as are cockroaches and household ants. So normal and expected is its early attack on imported furniture that many intelligent and otherwise well-informed people are convinced that it is already present in their mail-order purchases from continental sources. It is indeed true that no commercial cabinet wood of the Temperate Zone is immune from attack by dry-wood termites, but dry-wood termites do not exist where such woods are used for the construction of furniture.

Most unfortunately, the latest developments make it impossible for even local manufacturers to obtain the genuine mahogany, *Swietenia mahagoni* Jacquin, which has long been known as most resistant to infestation and thus most desirable for tropical furniture. The abundantly available Mexican or Honduran mahogany, *S. macrophylla* King, admittedly a real mahogany, is of the same genus as the endemic West Indian species, but its heartwood contains in only minute quantity the essential constituent which makes *S. mahagoni* so invaluable for permanence in the Tropics. Even more susceptible to termite attack are other woods which superficially resemble mahogany in appearance and to which this name has been applied: Philippine mahogany (so-called), *Shorea negrosensis* and other commercial species of *Shorea* and African mahogany (so-called), *Khaya ivorensis* and other commercial species of *Khaya*. Finally and most recently, Dutch mahogany, *Virola mycetis* Pulle (= *V. surinamensis* (Rol.) Warb.), locally in

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Surinam called Baboen or Baboonhoodoo, has appeared on the market in Puerto Rico. It is being extensively used by local cabinetmakers before the general public can realize the extent of the deception.

Many tropical heartwoods of the Amazon region are very resistant to termite attack, but are practically unknown and are commercially unavailable in Puerto Rico. Some native Puerto Rican woods, such as maga, sapo, palo de hierro, almendrón and guayacán, are superior to mahogany in their resistance to termite attack, but are present in such limited quantity that their extensive use in furniture construction is commercially impractical. But any wood whatsoever may be rendered absolutely, or at least superficially immune to termite attack by impregnation with suitable chemicals. To determine what these chemicals are, and which will prove to be most permanently effective in preventing attack by the West Indian dry-wood termite, *Cryptotermes brevis* Walker, is of vital economic importance to every householder in Puerto Rico. The manufacturer of furniture, both here and outside Puerto Rico, should by rights make the treatments to the termite-susceptible woods he uses before they ever reach the ultimate consumer, but the basic facts must be made available before he can take effective action. The results of extensive tests conducted by the Division of Entomology of this Station indicate which are these most effective chemicals. It is the purpose of this paper to report them.

"Graveyard tests" of stakes, using a few such chemicals for determining the effectiveness and permanence of their protection against subterranean termites, and against rot and decay, have been made elsewhere. Dry-wood termites differ so greatly in their habits and especially in their habitat, that such tests against the subterranean species are merely suggestive. Conversely, the tests of chemicals against dry-wood termites here reported must not be considered applicable to lumber exposed to the elements or buried in the soil. The dry-wood termites live under the same roof as man; they perish under exposure to heavy rain or hurricanes quite as surely as his furniture is ruined by exposure to the elements. Even if the chemicals found most permanently repellent to dry-wood termite attack are not water-soluble, their citation below is not necessarily a recommendation or even a suggestion of desirability for outdoor exposure, or underground burial.

To the sufferers from termite attack who contributed their about-to-be discarded furniture for conducting these tests, the writer is most profoundly grateful, for an abundant supply of experimental animals was quite as important as of chemicals to be tested. To those persons who contributed the often unpurchaseable experimental chemicals, he is also greatly indebted. They are: William Higburg, Reilly Tar & Chemical Corp., Indianapolis, Ind.; M. A. Warnes, E. O. Rhodes, and J. N. Roche, Koppers

Co., Inc., Orrville, Ohio; Ira Hatfield, Monsanto Chemical Co., St. Louis, Mo.; Frank B. Smith, Dow Chemical Co., Midland, Mich.; Harry F. Dietz, E. I. du Pont de Nemours & Co., Wilmington, Del.; Friar Thompson, Jr., Hercules Powder Co., Wilmington, Del.; Milton Goll, Nuodex Products Inc., Elizabeth, N. J.; Harry G. Walker, Whitemarsh Research Laboratories, Pennsylvania Salt Manufacturing Co., Philadelphia, Penn.; R. E. Kremers and H. K. Barnes, Central Laboratories, General Foods Corp., Hoboken, N. J.; W. E. Dove, U. S. Industrial Chemicals (for Dodge & Olcott), Baltimore, Md.; E. E. Gilbert, Laurel Hill Research Laboratories, General Chemical Division, Allied Chemical & Dye Co., Long Island City, N. Y.; F. L. Seanz, Mallinkrodt Chemical Works, New York, N. Y.; John Galaba, Niacet Chemicals Division, U. S. Vanadium Corp., Niagara Falls, N. Y.; H. R. Tisdale, American Dyewood Co., New York 16, N. Y.; John G. Dean, Mellon Institute of Industrial Research (for International Nickel Co.), Pittsburgh, Penn.; J. G. Saunders and Rogers W. Roth, Commercial Solvents Co., New York 17, N. Y.; H. H. Glass, F. W. Berk & Co. Inc., Woodridge, N. J.; W. G. Bywater, S. B. Penick & Co., New York 7, N. Y.; Ralph E. Heal, Merck & Co., Rahway, N. J.; Donald F. Starr, S. B. Penick & Co., New York 7, N. Y.; H. Douglas Tate, Naugatuck Chemical Co., Naugatuck, Conn.; C. C. Alexander, Geigy Co. Inc., Research Laboratory, Bayonne, N. J.; Julius Hyman, Julius Hyman & Co., Denver, Colo.; M. D. Leonard and W. E. McCauley, Agricultural Chemicals Division, Shell Chemical Corp., Denver, Colo.; F. C. Craighead, Forest Insect Investigations, Forest Service, U.S.D.A., Washington, 25, D. C.; M. L. Wolfrom, Department of Chemistry, Ohio State University, Columbus, 10, Ohio; Holger Erdtman, Division of Organic Chemistry, The Royal Institute of Technology, Stockholm 70, Sweden.

#### MATERIALS AND METHODS

Over 10 years have elapsed since the first tests began in Puerto Rico on the effectiveness and permanence of organic chemicals for the protection of wood against attack by the West Indian dry-wood termite, or "polilla". At that time, an abundant supply of West Indian birch lumber, or "almácigo", *Bursera* (or *Elaphrium*) *simaruba* (L.) Sarg., was available in the laboratory from another experiment, from which lathlike strips a quarter of an inch thick and an inch wide were cut, and left to air-season in the laboratory. These strips were cut into sections  $1\frac{1}{4}$  inches long as they were needed for tests. These were sandpapered on all sides, and the edges and corners beveled and rounded so that any feeding of the termites would be readily apparent. "Almácigo", as compared with other woods, was subsequently assigned the low termite-resistance rating (2)<sup>2</sup> of 23, the lowest for any

<sup>2</sup> Numbers in parentheses refer to Literature Cited, p. 149.

wood being 20. Figure 1 shows how the wood blocks were tested. Thus it was considered that if any chemical could protect samples of treated "almácigo" from termite attack, it would certainly be effective when applied to any other wood with a higher termite-resistance rating.

In tests during later years, "almácigo" wood was replaced with flamboyán wood, which has a termite resistance rating of 20, the lowest of any wood readily available in Puerto Rico. Flamboyán, or "Royal Poinciana", *Delonix* (or *Poinciana*) *regia* (Bojer) Raf., has been extensively planted along the roads of Puerto Rico, as well as just inside the boundary wall of

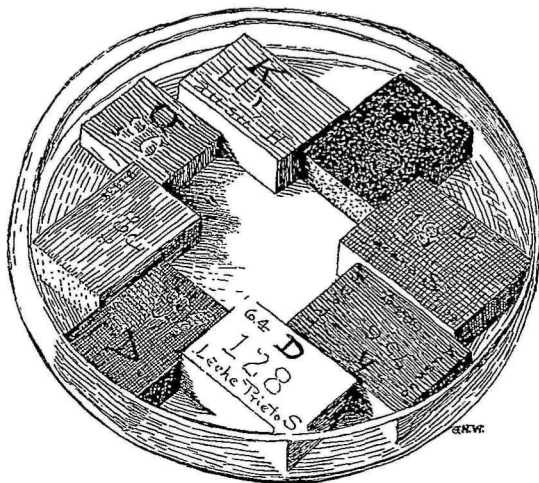


FIG. 1.—Testing wood samples for termite resistance. Drawn by G. N. Wolcott. (Original.)

the house of the writer, because of the magnificent display of its flowers during the summer. Its wood had no commercial value, and if it were not possible to induce a "caminero" (highwayman or road-tender) to contribute a section of the trunk of a flamboyán tree which he had cut down for firewood for heating a drum of tar to be used in road repairing, one could always sacrifice a tree out of one's own yard. Thus an extensive and easily renewed supply of wood blanks of a most termite-susceptible wood was assured for the entire further course of the tests.

The first important chemical tested was pentachlorophenol. Because it was first, tests in subsequent years with other effective chemicals can never catch up with it in proof of its superior permanence. The large sample of the chemical, which rather unpromisingly looked like poorly ginned cottonseed, contributed by the Monsanto Chemical Co. of St. Louis, Mo., some

years previously, was opened on January 18, 1944, and 1 gm. was weighed out to make a 2-percent solution in 50 cc. of benzol.

Three air-seasoned blanks of almácigo were given a final sandpapering before the one marked in India ink "2-percent pentachlorophenol" was submerged in the liquid. To ensure complete submergence the container for the liquid was only slightly more than an inch in diameter, and the almácigo blank was tied to the end of a glass rod with a cotton string so that its lower end rested on the bottom of the container, and its top end was half an inch or more below the top level of the liquid. The glass rod could be twirled between the fingers to dislodge any air bubbles from the submerged wooden block both at the beginning and at the end of the 10-minute period of complete submergence. After the first block had been impregnated with pentachlorophenol at 2 percent for 10 minutes and removed from the solution, this was diluted to 1 percent, the sample marked "1-percent pentachlorophenol" was placed in the liquid, and subsequently a block marked "0.5-percent pentachlorophenol" was immersed in a further dilution. The treated blocks of wood removed from the liquid after 10 minutes submersion were placed on the sill of an open window to dry in the sunshine, the concavity of the painted metallic sill accidentally being so formed that only two corners and an edge of the block were required for contact to hold it firmly in place for the free circulation of the air around it while the solvent evaporated. An hour or more after being thus exposed in the sunshine the treated blocks were placed on end in a petri dish and put on a top shelf until the following day (fig. 2).

The size of the blocks of wood had been carefully planned so that nine of them would just fit when arranged flat in a 145 x 15 mm. petri dish, using eight treated blocks, and if desired, in the center, one of West Indian mahogany (*Swietenia mahagoni* Jacquin), which has a termite-resistance rating of 80, for check. (See fig. 1.)

On January 20, 1944, the 1-percent-pentachlorophenol block was placed with other treated samples and mahogany in such a petri dish, together with numerous fresh termites removed from an infested desk. The petri dish was wrapped in a towel and placed on a shelf in a windowless constant-temperature oven set at 90°F. By the following day, most of the termites were on the mahogany, getting as far away as possible from the 1-percent pentachlorophenol-treated sample. On January 22, 22 termites were dead, their dead bodies being mostly on or around the pentachlorophenol block, which very obviously was toxic to them at that time and concentration of the chemical.

Then a fresh solution was prepared and almácigo blocks were impregnated at 0.2 percent and 0.1 percent. By January 29, the 0.1-percent-treated sample had been attacked by termites, and by January 31, so had the one

treated with the 0.2 percent of pentachlorophenol. But, although repeatedly tested, it was not until the following October that the 0.5-percent pentachlorophenol-treated sample was attacked. On December 21, 1944, the sample treated with 1 percent of pentachlorophenol showed signs of being eaten, but was left in place in the test so that the gouge might become unmistakable. On January 6, 1945, the sample was removed from the test, although the gouge was not much deeper. It has been repeatedly tested since, but although termites may rest on it in numbers when no other sample is more attractive, none has eaten it in the succeeding 9½ years. Long ago its entire back side has been filled with the penciled dates on

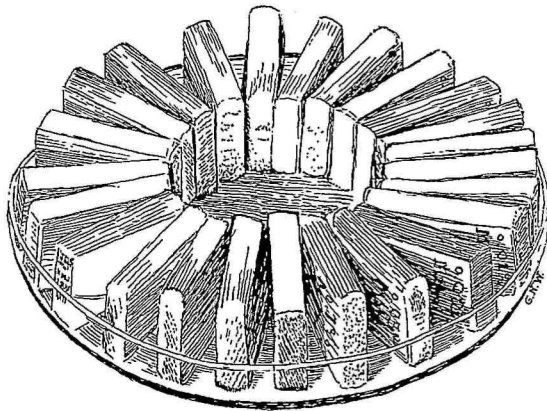


FIG. 2.—Method of stacking blocks of wood after impregnation to ensure maximum exposure for volatilization of chemicals. Drawn by G. N. Wolcott. (Original.)

which it was removed from tests during which it had not been eaten. Thus, so far as the West Indian dry-wood termite is concerned, it may be considered that submersion in a 1-percent solution of pentachlorophenol should give almost perfect protection against attack to any kind of wood, and that the 5-percent solution commercially used has a very ample margin of error for the application of this chemical.

The steps taken in testing pentachlorophenol have been related in detail, not only because of the intrinsic importance of this chemical, but because a somewhat similar perfected procedure was adopted as routine in the testing of other chemicals, with possible minor improvements in technique as the investigation proceeded. Thus, initial impregnations at 2, 1, 0.5, 0.2, 0.1, and 0.05 percents were standard for the great bulk of the chemicals, from which deviation was made only when the very small sample of chemical available for testing made necessary the use of an initial solution at a

smaller concentration, and greater dilutions to 0.02, 0.01, 0.005, and in some cases, even 0.002 percent.

The smoothest and most polished side of the wooden block was used for labeling. The label was written in India ink just before submergence in the solution of the chemical. The termites ate or disregarded the label in India ink as though it were not there, thus its presence in no way affected the results of the tests. The label as written at the top of the front face of the block showed the concentration of the chemical. Below that came the name of the chemical, and finally towards the bottom, the date of treatment, the back side of the block being reserved for later pencil notations of the date on which the sample was attacked, or the dates when it was temporarily removed from the tests uneaten. It was found desirable to have the writing of the label cover as much of the face of the block as possible, for in this way even the smallest disturbance of the letters or figures at once became apparent. Such very slight attacks were ordinarily not considered final or conclusive. To make sure of a major gouge or gouges, or tunnel or incipient tunnel, being eaten by the termites, the sample was continued under test until there could be no doubt that it had been attacked. That all the termites were noted resting on a sample was by no means convincing evidence that they were eating it: The block must show a definite gouge or tunnel, preferably through some letters or figures of the label.

The same glassware, the same glass rods, the same kind and size of wood blocks for impregnation, the same time and procedure for impregnation and subsequent exposure of samples for volatilization of the solvent, and subsequently of the much slower volatilization of the chemical itself when exposed in the air, were used for all chemicals that the results might be entirely comparable. Possibly a longer time of exposure, and especially pressure impregnation, would show a longer period of resistance to termite attack, and perhaps more closely approximate commercial procedure. But from the standpoint of prompt elimination of valueless chemicals, the minimum impregnation shortened the total time necessary for completing the investigation, and gave a fair, and it is hoped an impartial, standard of comparison for all the chemicals tested.

The problem of keeping so many small wood samples amply exposed to the air, so that volatilization of the chemical itself from the sample might be comparable to that which might be anticipated from furniture or interior trim, proved to be more difficult. For several weeks after the initial impregnation of a series of wood samples with a chemical, all uneaten samples (except those being tested) were left standing on edge in circles buttressed against the side of the petri dish and looking like a miniature Stonehenge (see fig. 2). But they could not be kept thus indefinitely.

The too zealous activities of the laboratory janitor made such exposure

impossible. The samples were too easily toppled over like rows of dominoes, and the petri dishes and shelf space were needed for the fresh series of samples treated with other chemicals. Eventually, those uneaten were laid away in termite-infested insect-display cabinets, the most heavily impregnated by each chemical on the bottom of the pile, and the least impregnated on top. The glass-topped display cabinets had been so largely destroyed by insect attack as to be entirely gone on one side; thus the free circulation of outside air around the sample was not impeded, even if it were not exactly stimulated.

As attacked samples accumulated, the initial small insect-display cabinet, which had been ample to contain them at first, was replaced with one very much larger, and as this became termite-infested, its contents furnished a supply of live termites for experimentation when all other sources, such as discarded furniture of friends and family, failed. The eaten blocks of wood, once the very thin, outer layer of chemical impregnation had been broken and passed, were, of course, as desirable to the termites, and as susceptible to attack, as untreated *almácigo* or *flamboyán* lumber. Moreover, one can shake the termites from them into an open petri dish without mechanical injury quite as easily as from infested plywood sheets of infested radio cabinets, and much more easily than from the wooden members of furniture that has to be chopped apart with a machete. The hollowed-out wood samples when removed from the large insect-display cabinet formed readily portable examples of termite injury that could be presented to interested visitors, or used for sending insect specimens or individual glass vials of insects as airmail enclosures.

The selection of additional chemicals for test was a matter of development as experience or accident over the years seemed to indicate profitable leads, and from the very nature of the investigation could not have been planned in advance. We commenced by testing the pure constituents of coal-tar creosote, contributed by Reilly and Koppers, none of which proved to be as effective as the crude creosote itself. Numerous chlorinated and other phenols were tested for comparison with pentachlorophenol, some purchased from Eastman, but others contributed by Monsanto and Dow. The experimental laboratories of other manufacturers, such as Laurel Hill of General Chemicals, and Whitmarsh of Penn Salt, hopefully submitted numerous samples of experimental chemicals. Because of their resistance to the attack of marine borers, many naphthenates and other compounds of naphtha were tested, mostly submitted by Nuodex Products of Elizabeth, N. J. When weed-killers were first being tested in Puerto Rico, A. S. Crafts of the Davis, Calif. Agricultural Experiment Substation, suggested trying some of the dinitro compounds that he had found most toxic to plants. All the new insecticides were tested before they had been named and while



they were still represented merely by manufacturers' code numbers, despite full recognition of the fact that the qualifications for effectiveness and permanence in impregnating woods to repel the attack of termites are quite different from those for insecticides.

As tests for many years previously had been and were continually being conducted on the natural resistance of woods to termite attack, it appeared logical that an important source of termite-repellent chemicals should be one or more extractives of the woods known to be termite resistant, or similar compounds. This presumption, based on the proved value of  $\beta$ -methyl-anthraquinone, or "tectoquinone", an extractive of East Indian teak, *Tectona grandis* L., turned out in this case to be a blind alley, for not one of the commercially available quinones tested, and only a few of their metallic lakes prepared by Yolanda Pirazzi of the laboratory of the Department of Chemistry, proved to be as termite-resistant as tectoquinone itself. All of the other extractives of wood which could be obtained from commercial sources, proved to be valueless.

At this juncture, the whole-hearted cooperation of Holger Erdtman of the Royal Institute of Technology, Stockholm, Sweden, made successful progress possible. Other European researches had demonstrated the toxicity to wood-decaying fungi of the extractives he was obtaining from coniferous woods, and he generously contributed ample samples of these experimental chemicals for tests with termites. Furthermore, being familiar with what other widely separated chemists were accomplishing in the extraction and identification of wood constituents of deciduous trees, he sent a sample of chlorophorin prepared by F. E. King of Nottingham University, England, from a species of *Chlorophora* similar to the dye-wood "mora" of Puerto Rico. He suggested to M. L. Wolfrom of Ohio State University that the extractives he was obtaining from Osage orange, *Maclura pomifera* (Raf.) Schneider, should be tested for termite attack, as our tests with the wood itself had shown it to be the only termite-resistant wood of all Temperate Zone North America, excepting only very gummy southern cypress.

## RESULTS

### BASIS OF COMPARISON

After having considered several possible arrangements for presentation of results, and having discarded tables, the alphabetical method, or grouping by chemical affinity, as used in a previous publication (3), it seemed desirable to be guided mainly by the permanent effectiveness of the chemical in protecting wood from termite attack. Those chemicals least valuable for the purpose are listed first, and gradually as the end of this section is approached, those which seem most desirable are discussed in greater detail.

This is simple enough at first, but subsequently becomes more compli-

cated. For instance, many chemicals were unavailable in quantities that could be used for impregnation at concentrations of 0.5, 1, or 2 percent, and it is impossible to extrapolate with any great confidence what unexpected qualities they might have displayed at greater concentrations. Yet, because any chemical that continues to render the block continually resistant at a 0.5-percent dilution is by that much superior to pentachlorophenol, that has been made the point of division. Blocks impregnated with pentachlorophenol were eaten at 0.5 percent, and after an initial gouge was made in the sample impregnated with 1-percent pentachlorophenol, they later proved continuously resistant. From the standpoint of termite resistance all chemicals are judged as "not so good as pentachlorophenol", or the very special few "apparently better than pentachlorophenol".

#### THE LESS EFFECTIVE CHEMICALS

As was indicated by the reactions of the termites attacking wood impregnated with some of the least resistant chemicals, such common solvents as petroleum ether, benzol, alcohol, acetone, and water volatilized so completely within 24 hours after submersion that all traces of them completely disappeared. Pyridine, a coal-tar product supplied by Reilly, sometimes used as solvent, did not, however, volatilize so rapidly, and 3 days elapsed before the termites started eating the sample of almácigo wood submerged in 100-percent pyridine. Its characteristic odor, so offensive to us, may not be apparent at all, or in the same way, to the termites. Indeed, one should beware of judging anthropomorphically the value of any suggested termite-repellent on the basis of how horrible its odor may seem to man's senses of taste or smell. Of other liquid coal-tar constituents contributed by Reilly, 2,6-lutidine protected wood 4 days, and pure  $\alpha$ -picoline only 5 days. Commercial phenol, or carbolic acid, protected the sample in which it was submerged for 32 days, but that dipped in 2-percent phenol was eaten the following day. A sample impregnated with 2 percent of 2,6-bromophenol was eaten in 5 days, and with *p*-bromophenol in 7, but the 2,4-bromophenol protected it 16 days. Submersion in a sample of undiluted liquid orthochlorophenol, submitted by Monsanto for comparison with their pentachlorophenol, protected a sample against termite attack for 13 days.

Plastic cellulose acetate proved to be more attractive to the termites than the wood on which its film was deposited, the 2-percent film being eaten off in 2 days, with the wood underneath untouched so long as there was any more plastic to eat. Both styrene dibromide and polyvinyl acetate (duPont) were also more attractive than almácigo wood, and the plastic polystyrene, contributed by Dow, at 2 percent resisted attack only 12 days. Dow's Saran, a polymerized vinylidene chloride, produced a much more termite-

resistant film, which applied undiluted at 20 percent, was not broken through by the termites for 1 year and 10 months.

Pine Oil No. 91 of the American Turpentine and Tar Co., New Orleans, La., gave no protection against termite attack, the samples with a 2-percent impregnation being eaten in 2 days. A sample impregnated with cedar oil (Central Scientific) at 2 percent was eaten in 3 days. Yarmor No. 302 pine oil of Hercules Powder Co., and their  $\alpha$ -terpineol, at 2 percent protected samples for 6 days, but submerging in the latter undiluted protected for 92 days.

Of the solid coal-tar constituents contributed by Reilly, the 2-percent impregnations of quinoline, chrysene, and *m,p*-cresol were attacked in 7 days. Acenaphthene, fluorene, and carbazol, contributed by Koppers, and 1,3,5-xylol of Reilly at 0.5 percent protected the blocks for only 3 to 5 days; at 2 percent, the carbazole-impregnated block was eaten in 14 days, the one impregnated with 1,3,5-xylol in 54 days, with acenaphthene in 62 days, while the fluorene repelled attack for 73 days. The following chemicals at a 0.5-percent impregnation were effective only for 5 days: 1,2-naphthoquinone, indigotin, 4,4'-dihydroxy-diphenyl, Reilly's Transote, sucrose octoacetate—a very bitter sugar from Niacet Chemical Corp. of Niagara Falls, N. Y., copaivic acid, diphenylene oxide (Reilly), diphenyl, styrene or vinyl benzene, and thiophenyl; and for 7 days: 2,6-dibromo-4-aminophenol, catechol, *p*-chloracetophenone, 9,10-dichloranthracene, the wood-constituent gambier contributed by J. S. Young & Co., Baltimore, Md., naphthalene tetrachloride, Koppers' phenanthrene, and hexachlorphenol.

Hexachlorphenol, which at 1 percent protected wood for 133 days, was effective at 2 percent for 10 years after impregnation. Thus, the additional chlorination, instead of making it more termite-repellent than pentachlorphenol, merely had the effect of requiring a greater concentration to be equally repellent. For comparison, blocks impregnated with pentabromophenol at 0.5 percent were eaten in 14 days, but the wooden block impregnated with 1 percent is still uneaten 10 years later.

Three experimental chemicals submitted by the Laurel Hill Laboratory of General Chemical Co.: Hexachlordiphenyl trisulfide, phenol monochloropotassium acetaldehyde, and dichloro-dihydro-anthracene, with which wood samples were impregnated at 0.5 percent afforded protection for only 8 or 9 days; the samples showed little greater resistance to termite attack at greater concentrations.

The following constituents of woods imparted so little resistance to termite attack that almácigo or flamboyán wood samples impregnated with them at a concentration of 0.5 percent were eaten in 8 to 10 days: Morin; pyrogallol; cashew nut-shell oil or Cardol, presented by Louis

Dejoie of Haiti; copper anacardate, prepared by the laboratories of General Foods; Terposol No. 8 and Hercolyn, a hydrogenated methyl ester of abietic acid submitted by Hercules Powder Co.; fustic, contributed by J. S. Young & Co. of Baltimore, Md.; resorcinol, and vanillin. Not one imparted much greater resistance at 1 or 2 percent, and all may be considered valueless in repelling termites. Indeed, Bengt Leopold, working in Erdtman's Organic Chemistry Laboratory of the Royal Institute of Technology at Stockholm, Sweden, found that the dark, amber-colored excrement of drywood termites which had been eating Douglas fir contained 13 percent of vanillin, and estimated that if such a vanillin-rich excrement were available in commercial quantities it would be worth \$50 a ton as a source of vanillin!

When the gamma isomer of benzene hexachloride or hexachlorocyclohexane was not commercially available, a mixture of the alpha and beta isomers could be obtained from Eastman. This mixture of the isomers at 0.5 percent prevented termite attack for only 10 days, at 1 percent for 15, and at 2 percent for 44. The gamma isomer, supplied by duPont when it was still a chemical curiosity, even at a 0.01-percent impregnation imparted resistance to attack for 136 days and had a regular curve to 259 days at 0.5, and 303 days at 1 percent, which was the greatest concentration at which the minute sample could be impregnated.

The chemicals which at 0.5-percent concentration of impregnation protected samples from termite attack for 11 days (or less) were: Dibromonaphthalene, 2-chloro-6-nitrotoluene (duPont), chloramine T (chlorazone 1,4), di-(2,4-dichlorophenyl) carbonate (Laurel Hill), rufigallol, 2,4,6-tribromophenol, phenyl salicylate, 4,4'-dichlorobenzophenone (Dow), polymerized methyl methacrylate, 4,4'-dibromodiphenyl, and L-rhamnose hydrate; for 13 days: Laurel Hill experimental chemicals such as a condensation product of potassium acetaldehyde disulfonate and T-butyl-phenol and the monochlor of the same, 4-chloro (2-phenoxy) benzoate, hexachloracetone, phenol potassium acetaldehyde disulfonate, a distilled neutral 50-percent fraction of cardol supplied by General Food Laboratories, sodium tetrahydronaphthalene- $\beta$ -sulfonate, oxine, 8-hydroxyquinoline, resorcinol monomethyl ether, hematoxylin, and diphenyl triketone. The only one of these chemicals notably more resistant to termite attack at greater concentrations was diphenyl triketone, which at 2 percent was not finally eaten until after 497 days.

To the uninitiated it would seem that if a phenolic compound were termite-repellent, a diphenol would be twice as repellent. Tests disproved this. Wood samples submerged for 10 minutes in 0.5-percent diphenylene oxide were eaten in 3 days; in 0.5-percent diphenyl in 6 days. The clear, sparking series of diphenyls, called "Aroclor" by Monsanto, proved to be

very much of a disappointment, for the termites ate the treated samples so greedily as to leave no doubt. The flamboyán block submerged for 10 minutes in 0.5 percent of tetrachlordiphenyl was eaten in 10 days; of pentachlordiphenyl in 12 days; of hexachlordiphenyl in 21 days; of its trisulfide in 8 days; of heptachlordiphenyl in 12 days; of decachlordiphenyl in 8 days; of nonachlorterphenyl in 19 days. No blocks impregnated with greater concentrations proved to be much more resistant.

The 2-amino-xanthone and 2,7-diamino-xanthone from Laurel Hill proved to impart less resistance to termite attack than xanthone itself, the samples impregnated with 0.5 percent being eaten in 15 days. The mosquito- and punkie-repellent chemicals manufactured by Dodge & Olcott: Caryophylene and "Dimelone" (dicyclo-(2,21)-5-heptene-2,3-dicarboxylic acid, dimethyl-ether), lacked permanence under exposure to the air, and the impregnations on wood samples at 0.5 percent were eaten by termites after 16 to 17 days, greater concentrations being little more effective. A heavy chlorination of crude anacardic acid prepared by General Foods proved no more permanently repellent. The  $\beta$ -chlor-anthraquinone impregnation at 0.5 percent was attacked in 16 days, but the 2 percent resisted for 178.

The following chemicals in impregnations at 0.5 percent resisted termite attack for not more than 15 to 18 days: Saponin, a wood constituent supplied by S. B. Penick & Co.; 2,4-dichlor-phenoxy-acetic acid (duPont); 2-chlor-orthophenyl-phenol (Dow); carbostyryl, or 2-hydroxy-quinoline; nickel pentachlorphenate, contributed by International Nickel Co.; Lederle's sulfanilamide (*p*-amino-benzene-sulfonyl-amide), zinc lake (OH) of quinizarin, *p,p*-difluorodiphenyl, sodium tri-iso-propylnaphthalenesulfonate. An 18-percent chlorinated crude cashew nut-shell oil synthesized by General Foods, and guaiacol, presumably extracted from the heartwood of *lignum-vitae*, *Guaiacum officinale* L., but obviously not the constituent responsible for its complete resistance to termite attack, gave protection for 21 days.

A 0.5-percent solution of Lederle's sulfathiozole protected wood only 23 days against termite attack, as did quinone, pentachloracetone, triphenyl phosphine, quinihydrone, and Dodge & Olcott's phenol B.; a 0.5-percent impregnation of Naugatuck's Chloranil (tetrachlor-para-benzoquinone) protected wood 25 days, and a 2-percent only twice as long. Two coal-tar constituents submitted by Reilly were much more effective at greater concentrations, pyrene at 2 percent imparting resistance for 195 days and fluoranthene for almost a year, but phenanthrene (Koppers) only 87 days.

The Osage orange crystals manufactured by the Taylor, White Extracting Co. of Camden, N. J., apparently contain very little of whatever con-

stituent of Osage orange wood is responsible for its resistance to termite attack, for impregnations with a 0.5-percent solution prevented termite attack for only 27 days, and with 1 percent for 33. Quinalizarin and the zinc lake (OH) of anthrarufin and chrysazin showed no greater promise, nor did 3,5-dinitrosalicylic acid or 2,4-dihydroxydiphenyl, sodium 2,6-dibromobenzononeindo-3-bromophenol, pentachloronitrobenzene (Laurel Hill), or the copper lake of Eastman's dihydroxyanthraquinone.

Copper naphthenate, extensively used for the protection of the bottoms of wooden ships and boats against the attack of marine worms, is of little value against dry-wood termites. It is a very dark-green, foul-smelling, sticky liquid, but impregnation with a 0.5-percent solution prevented termites eating the samples only 28 days. Although the 1-percent impregnation held out for 150 days, only the 10-percent gave complete protection. If it seems incredible that the termites minded it so little, it must be remembered that their senses of taste and smell are quite different from ours, and what seems extremely offensive to us may not produce the same reaction in them.

The commercially unobtainable catechin, supposedly a decay- and insect-repelling wood constituent, was eventually received from General Foods as *l*-epicatechin, but the 0.5-percent impregnation resisted termite attack only 29 days, and the 1-percent, 31 days. Their sample of anacardic acid was also disappointing. Similarly valueless were bis-(1,2,3-trichlorophenyl) methane and perchlorhydrindene from Laurel Hill, benzophenone, triphenyl phosphite, and the wood constituents thanite (Hercules Powder), linalool, and brucine. Because glossy paper coated with aluminum sulfate is discriminated against by termites when uncoated paper is available, high hopes and great expectations attended the tests with aluminum pentachlorophenolate, supplied by Dow, but it was no better than dicyclohexamine pentachlorophenolate, neither being even measurably comparable in repelling termites to pentachlorophenol itself.

Termites ate the flamboyán wood impregnated with 0.5-percent anthragallol in 33 days, and that with 2-percent in 66. The Eastman preparation of saponin gave results closely paralleling those with saponin from another source, and impregnations with their 3-bromo-ace-naphthene was also eaten at 0.5 percent in 33 days. Before the chemists had learned how to synthesize pentachlorophenol, tetrachlorophenol was the most heavily chlorinated phenol available. Its inferiority was shown when flamboyán was impregnated with a 0.5-percent solution of the sample supplied by Dow, and was eaten in 37 days, at 1 percent in 46 days, and at 2 percent in 116 days.

When DDT was just beginning to attract attention as used by the U. S. Army, a minute sample was obtained through the courtesy of F. C. Craighead of the Forest Insects Division of the then Bureau of Entomology and

Plant Quarantine, USDA. The sample of flamboyán wood impregnated with 0.5-percent DDT was eaten 35 days after submersion and with 1-percent in 38 days; but still uneaten over 10 years after the date when it was dipped in the chemical is the one impregnated with the 2-percent DDT. When termites do not like a sample, they often deposit liquid excrement on it; the 2-percent sample is almost covered with the spots, showing how little it was appreciated by them. In considering the use of DDT for commercial impregnation it should be noted that it is only half as repellent as pentachlorophenol, and that considerably more than a 2-percent solution should be used to give an ample margin of error.

Triphenyl stibine may be as effective as DDT, samples impregnated with its 0.5-percent solution not having been eaten for 45 days and the 1-percent for nearly 2 years (686 days). But no impregnation at 2 percent was prepared, and it remains untested at this concentration. The zinc lake (acetic acid) of anthragallol at 0.5 percent repelled attack for 37 days, and at 1 percent for 90; the copper lake of anthragallol repelled attack for 44 and 134 days, but neither was tested at greater concentrations.

Indeed, it is really rather pointless to carry tests beyond the concentration at which pentachlorophenol imparts resistance, and also many chemicals are little more repellent at the greater concentrations. For instance, the impregnation of anthraquinone at 0.5 percent was eaten in 43 days, the 1 percent was eaten on the very next day, and the 2 percent 2 days later. Samples impregnated with 0.5-percent solutions of two experimental chemicals submitted by the Laurel Hill Laboratories, hexachlorocyclopentadiene dicyclopentadiene and a highly chlorinated adduct of monochloropotassium acetaldehyde disulfonate with phenol, were eaten in 39 and 43 days, respectively, and were only somewhat more resistant when impregnated with greater concentrations. Pentachlorophenyl laurate submitted by Monsanto proved slightly more repellent, but its 2-percent-solution impregnation was attacked in 128 days. A mixture of 65 percent of 1,5-dihydroxyanthrarufin and 35 percent of 1,8-dihydroxychryszazin (Eastman), when dissolved in lutidine and used in 0.5-percent solution to impregnate flamboyán wood prevented attack for 48 days, but dissolved in sodium hydroxide, the 0.5-percent impregnation was eaten in 4 days, and the 1-percent in 10.

When chlordane was so new that only a small experimental sample could be furnished by Dow, the 0.01-percent dilution made the wood sample initially toxic and killed all the termites in the test, but after a 2-week exposure in the air it was no longer toxic, and the samples were eaten at increasingly greater concentrations up to 0.5 percent in 48 days. The 1-percent-solution sample was not attacked for over a year, and the 2-percent impregnation proved repellent for 378 days. The sample of 4-chlor-

benzophenone submitted by Dow was not toxic at all and blocks on which it was used were promptly attacked at the lower concentrations, but were exactly as resistant at 0.5 percent as if impregnated with DDT, and less so at 1 and 2 percents.

Isothymoxy chloroethyl ether, the solvent C of Dodge & Olcott, proved to be more repellent to termites than most chemicals that it might be used to dissolve, the impregnation at 0.5 percent not being attacked in 53 days, and at 2 percent for twice as long.

The following chemicals at 0.5-percent-solution impregnations made flamboyán wood samples resistant to termite attack for over 50 days, but were little more repellent at greater concentrations: Phenanthrene quinhydrone, hexaethyl tetraphosphate (Monsanto), quinizarin or 1,4-dihydroxyanthraquinone, a Penn Salt glycol (alkyd) resin of 2,3,4,5-tetrachlorophthalic anhydride, the copper lake of alizarin, and the least repellent two of a series of benzalaniline compounds synthesized in the organic chemistry laboratories of the Royal Institute of Technology, Stockholm, Sweden, and sent by Erdtman: 3,4-dimethoxybenzalaniline and 2,3,4-trihydroxy-benzalaniline.

A 0.5-percent solution of the dinitro-o-phenyl phenol submitted by Dow gave immunity to termite attack to the sample of flamboyán wood impregnated for 69 days; the 1-percent sample is still unattacked. On the basis of our tests, and insofar as the West Indian dry-wood termite is concerned, this chemical is as good as pentachlorophenol and has the additional advantage (or disadvantage) of deeply staining the light-colored wood sample an intense yellow, so that one may be assured that the wood has been adequately covered on every visible part of its surface. Not so attractive in appearance is the Dow experimental textile fungicide, K-4639, a cupric salt of 3-phenylsalicylic acid, which when dissolved in benzol is a densely dark-brown solution lightly staining light-colored woods. Impregnation with 0.5-percent solutions protected flamboyán wood for 79 days; the 1-percent samples had not been eaten 6 years later. On the basis of our tests it too may be considered as practically equivalent to pentachlorophenol in protecting against the attack of the West Indian dry-wood termite.

Many other chemicals which repel termite attack at impregnations of 0.5 percent provide little more resistance at 1 percent and greater concentrations. The Naugatuck experimental chemicals 2,3-dichlor-1,4-naphthoquinone and 2,3-dichlor-naphthoquinone with sodium isothiocyanate at 0.5 percent provided protection for only 74 to 78 days, and at 2 percent slightly less than twice as long. Samples impregnated with Laurel Hill's 2,2-di(4-hydroxy-3,5-dichlorphenol) propane, dichlorxanthone, and chloral 4-chloraniline at 0.5 percent were eaten in 71, 75, and 79 days, respectively.



At greater concentrations the chemicals repelled attack for not much longer periods.

Impregnations with 0.5-percent solutions of chrysin (5,7-dihydroxy-flavone), a constituent of *Pinus lambertiana* Douglas, extracted in Erdtman's laboratories in Sweden, repelled attack by *Cryptotermes brevis* for 55 days, but in less than twice as long a period samples impregnated with it at 1 percent were eaten. Alizarin (1,2-dihydroxy-anthraquinone) similarly imparted resistance for months at low concentrations, but in less than 4 months the deeply stained 2-percent impregnations were attacked, the termites on the day following such a meal showing the purplish color of their food right through the thin walls of their transparent abdomens.

Solutions of osajin, extracted from Osage orange, *Machura pomifera*, by M. L. Wolfrom of Ohio State University, and named and its chemical structure established by him, when used for impregnating flamboyán wood at such an extreme dilution as 0.002 percent repelled termite attack for 39 days. But, at 0.2 percent the sample was attacked in 61 days, and presumably osajin is little more repellent at the greater strengths which could not be tested because of the small sample submitted. A smaller sample of iso-osajin monomethyl ether proved to be even more repellent, repelling attack for 47 days at 0.002 percent, but at 0.1 percent the sample was eaten in 73 days. It is doubtful whether either it or osajin is the important constituent of Osage orange wood responsible for its termite-resistance rating of 90.

#### THE MORE EFFECTIVE CHEMICALS

Of the experimental chemicals submitted by the Laurel Hill laboratories, impregnations of a 0.5-percent solution of di-(4-hydroxyphenyl)2,2,2-trichlorethane imparted immunity to termite attack for 82 days, and for a little more than three times as long at 2 percent. Dibromoxanthone at 0.5 percent repelled attack for 83 days; trichlorethyl-trichlorvinyl sulfonate for 91, and chloranil cyclopentadiene for 95 days. Laurel Hill's 4-iodoxanthane, of which the 0.5-percent solution conferred immunity to termite attack for 124 days, has not yet been eaten at 1 percent, 6 years after impregnation. This is also true of their 2,4-dichlorophenyl-2-phenoxy benzoate, but unfortunately we had no sample of their 2-ethylhexyl-5-nitrosalicylate, attacked by termites at a 0.5-percent impregnation, for test at a greater concentration. Hexachlorcyclopentadiene-2,4-dichlor-phenylallyl repelled attack at 0.5 percent for 133 days; a benzoquinone reaction product with hexachlorcyclopentadiene prevented attack at 0.5 percent for 147 days; benzoyl xanthone prevented attack for 148 days; and penta-

methyl flavan for 157 days; but these also were not tested at greater concentrations.

The zinc lakes (acetic acid) of quinizarin and of  $\beta$ -chlor-anthraquinone were used to impregnate flamboyán wood samples in 0.5-percent solution, and both were attacked in 96 days, with the 1-percent impregnations immune to termite attack 8 years after treatment. A comparable similarity was shown by 3,4-methylene dioxystilbene and 3,4-dimethoxystilbene, experimental chemicals sent by Erdtman, of which the termites attacked the impregnations at 0.01 percent in 63 days for both chemicals; in 86 or 88 days at 0.5 percent, but took twice as long at 1 percent. No such detailed data are available on two other wood extractives sent by Erdtman, cedrol and the glucoside rhapontin for, attacked at the lowest concentrations after a few days, the 1-percent samples when left in termite-infested boxes for 15 months were found eaten when finally examined. A longer period of neglect for the 0.5-percent and 1-percent impregnations of  $\alpha$ -naphthoflavone, uneaten by the termites for a number of years and finally left undisturbed in a termite-infested display cabinet, is responsible for the lack of exact data concerning the period of something less than 9 years during which they continued resistant. Eventually deep tunnels were noted in the back. Pinoembrin (5,7-dihydroxy-flavonone), extracted from *Pinus lambertiana* Douglas in Erdtman's laboratory, was not nearly so repellent to termite attack, its 0.5-percent-solution impregnation being eaten in 107 days and the 1-percent in 288.

Tests with the very toxic sodium fluoracetate, Monsanto's "1080", resulted in the death of many termites. Nevertheless, they ate the samples impregnated with 0.5-percent solution in 107 days and with 1-percent in 167. This chemical is much too dangerous to use for wood impregnation since many comparatively innocuous chemicals are available which are merely repellent, and not toxic, and which are much better for this specific purpose.

The 3,5-dinitro-o-cresol impregnation with 0.5-percent solution protected wood from attack 96 days, and at 2 percent three times as long. Dinitro-sec-amylphenol imparted more permanent resistance, the 2-percent-solution impregnation not being attacked for 535 days. Ammonium-dinitro-ortho-sec-butyl phenol, of which "Sintox W" of the Standard Agricultural Chemicals Co., Hoboken, N. J., contains 12 percent, which was the source of the material for testing, impregnated with 0.2-percent solution repelled termite attack for 59 days, just the same length of time that the 3,5-dinitro-o-cresol repelled attack, but its 0.5-percent impregnation was not attacked by the termites in 6 years. At this dilution the chemical stains the wood treated a bright yellow, positive proof that its protective film covers all surfaces of the submerged lumber. This material is com-

mercially available in quantity, and on the basis of these tests, is preferable to dinitro-*o*-phenyl phenol, the other bright-yellow staining dinitro compound. A 0.5-percent solution of Dow's 4,6-dinitro-*o*-sec-butylphenol prevented attack for 244 days; at 1 percent the sample has not been eaten in 7 years.

Blocks impregnated with a 0.5-percent solution of isobornyl thiocyanacetate, contributed by the Hercules Powder Co., resisted termite attack for 132 days, but the 1-percent impregnation was eaten in less than twice that time. Dibenzyl, of which the impregnation at 0.5 percent was eaten in 121 days, was not tested at greater concentration because of the small sample sent by Erdtman. Physodic acid, available in greater quantity up to a 1-percent impregnation, survived in the tests for 162 days. Diphenyl octatetraene, also supplied by Erdtman, but for which no solvent was found at more than 0.1-percent concentration, prevented termite attack for 123 days on wood impregnated with the saturated solution.

Piperonyl butoxide, the triumph of Dodge & Olcott in their researches with pyrethrum, gave an immunity to termite attack in flamboyán wood submerged in a 0.5-percent solution for 181 days, in 1-percent for 229, and in 2-percent for 287. Samples impregnated with their piperonyl cyclohexenone at a 1-percent dilution were uneaten after over 7 years. Penn Salt's experimental chemical 2-ethylhexyl-2,3,4,5-tetrachloracetate, when used for impregnating flamboyán wood at 0.5-percent concentration, protected it from termite attack for 190 days. Obviously it was not tested at sufficient concentration to indicate whether it was in reality better than Laurel Hill's genicide acids, of which the 0.5-percent impregnation was attacked in 163 days, but the 1-percent is still uneaten after nearly 7 years. Laurel Hill's pentachlorophenyl diethyl thionphosphate impregnation, eaten at 0.5 percent and 1 percent, remained untouched at a 2-percent concentration after 5 years. A sample impregnated with diphenyl mercury at 1-percent concentration is still sound after nearly 9 years, and so is one impregnated with phenylmercuric chloride at 2-percent.

Impregnation with a 0.5-percent solution of 3,4-methylenedioxybenzal-aniline prevented termite attack on flamboyán wood for 204 days. This statement, independent of any explanation, seems rather pointless. Actually, this chemical is only one of a series of benzalaniline compounds prepared in the organic chemistry laboratories of Holger Erdtman with the idea that, on the basis of chemical analogy, some might prove more permanently repellent to termite attack than the wood extractives, pinosylvin, and stilbene. A preliminary and incomplete account of these results has already been published (4); this is a more complete summary.

Benzalaniline itself, in which nitrogen replaces one of the ethylene bonds of diphenylethylene or stilbene, is not as repellent to termites as is stilbene,

but the 0.5-percent-solution impregnation on flamboyán wood prevented attack for 318 days. Some of the compounds formed with it were much less repellent; the 3,4-dimethoxy at 0.5-percent giving protection against termite attack for only 52 days, and 2,3,4-trihydroxy for 53. As stated at the beginning of this paragraph, the next most repellent in the series is 3,4-methylenedioxy, for 204 days. The 2-hydroxy at 0.5 percent conferred immunity for 267 days; 3-methoxy-4-hydroxy for 272; 2-nitro for 294; 3-methoxy-4-hydroxy-5-chloro for 316; the 4-methoxy for 341; the 4-hydroxy for 357; the 4-chloro for 417; the 2-hydroxy-3-methoxy for 873; the 3,4-dihydroxy for 929; the 2,4-dichloro for 952 (or over 2½ years) but the 2,4-hydroxy permitted attack at 0.002-percent only after 257 days, and at 0.005 percent still produces immunity nearly 3 years after impregnation. Under constant test the sample shows no sign of being even attractive for the termites to rest on.

Azobenzene, in which nitrogen completely replaces the double ethylene bond of diphenylethylene, even at the greatest dilutions proved to be more repellent than benzalaniline, and after the termites had attacked the wood sample impregnated with a 0.02-percent solution in 142 days, they showed no interest in the 0.05-percent impregnation made nearly 3 years ago. Both benzalaniline and azobenzene are commercially available, and numerous experimental compounds with the former, besides those sent by Erdtman, have been tested against mites, ticks, and insect pests attacking man (1), but only one with azobenzene. By analogy, a 2,4-dihydroxyazobenzene would seem to be indicated as the ultimate in termite-resistance. The sample synthesized by the chemists of Nuodex International, courtesy W. J. Strossen, is bright crimson, staining flamboyán wood orange, and at lesser strengths, yellow. With tests just started, it proves to be not nearly as repellent as azobenzene, impregnations at 0.5 percent being eaten in 49 days. An impregnation in flamboyán wood with a 0.05-percent solution of the sodium salt of 2,5-dichloro-4'-hydroxy-azobenzene (Penn Salt) protected it less than a month, but the 0.1-percent impregnation remained untouched a year later. With the greatest difficulty, 2,4-dihydroxyphenanthrene (a dehydro cis-pinosylvin) was prepared in Erdtman's laboratory, and a wood sample with a 0.05-percent impregnation resisted attack for 594 days. Phenanthrene itself at an impregnation of 1-percent was attacked in 8 days.

Because a suitable solvent for salazinic acid was not found, the greatest concentration at which the wood sample could be impregnated was 0.1 percent. Initially very repellent at the greatest dilutions, a 0.002-percent film being resistant to the termites for 109 days, the 0.1-percent saturated-solution impregnation was eaten in 126 days. Vulpinic or lichen acid at 0.1-percent impregnation resisted attack for 159 days, and the 0.2-percent remained immune to attack 3 years after treatment. Equally resistant at

the greater dilutions was *d,l*-usnic acid, but the 0.5-percent-solution impregnation was eaten in 312 days, and the 1-percent in 467. Erdtman had sent these accompanying other wood extractives. The sample impregnated with 0.5-percent 1,5-dibromo-pinosylvindicimethyl ether was attacked in 213 days, and with the 1-percent in 403 days. Though the 0.5-percent impregnation proved to be resistant for over a year, the sample of 2,3,6,7-tetramethoxy-9-10-dihydrophenanthrene was too small for test at greater concentrations.

The major insect- and fungi-repellent constituent of Scotch pine, *Pinus sylvestris* L., supplied for these tests by Holger Erdtman of the Royal Institute of Technology at Stockholm, Sweden, was initially remarkably resistant to termite attack, flamboyán wood impregnated with pinosylvin at 0.01 percent remaining immune for 565 days in our tests. But subsequently, at greater concentrations, the impregnations proved less permanent, so that at 0.5 percent the wood sample was eaten in 670, and at 1 percent in 674 days. Pinosylvin is 3,5-dihydroxystilbene, and 0.5 percent of stilbene itself, a commercially available chemical, rendered the impregnated wood sample repellent for 826 days, and at 1 percent for 893 days, or somewhat more than 2 years. Other wood constituents, or some compounds synthesized from pinosylvin, are even more permanently repellent. The dihydropinosylvin monomethyl ether, of which the 0.5-percent impregnation resisted attack for 1,278 days, at 1 percent produced immunity for over 5 years. Pinosylvin dimethyl ether, of which the 0.2-percent impregnation was eaten in 577 days, is unattacked at 0.5 percent 3 years after impregnation. By far the most repellent of these wood constituents was pinosylvin monomethyl ether, of which the flamboyán sample impregnated at 0.01 percent remained untouched nearly 6 years later. Indeed, it is almost covered by the spots of dried liquid excrement with which the dry-wood termites eventually adorn a bit of wood unamenable to their voracity.

The flamboyán wood sample impregnated with 1 percent of 2,4,6-trinitrostilbene resisted attack for almost 4 years, and the 0.2-percent impregnation of 2,4,2',4'-tetranitrostilbene ceased to be immune after 2 years and 4 months. Wood impregnated with 0.1-percent solution of 2,4-dichlorostilbene was not eaten for 277 days, and the 0.2-percent is still uneaten. Most repellent of all are the 2,4-dinitro-2',4'-dichlor-stilbene, and 4,4'-dinitro-stilbene; the wooden samples impregnated with dilutions of 0.005 percent were uneaten after 4½ years.

The wood of the Australian cypress pine, *Callitris glauca* R. Brown, has such a horrible, penetrating, and persistent odor that even termites are repelled by it, and the wood has been given a termite-resistance rating of 100+. No sample of callitrol was available to Erdtman, but he was able

to obtain (plus)-citronellidene acetic acid which is a synthetic analogue of (plus)-citronellic acid. The termites could scarcely distinguish between the two, impregnations with a 1-percent solution being attacked in 561 to 569 days. This still does not indicate whether the minus extractive would be as comparably powerful in repelling termites as is the wood from which it is obtained.

The wood of Douglas fir, *Pseudotsuga taxifolia* (Poir.) Britton, is very susceptible to attack by *Cryptotermes brevis*, especially when available as plywood, and its heartwood has a termite-resistant rating of 55, its sapwood of 49. It is possible, however, that the extractive taxifolin (3,5,7,3',4'-pentahydroxoflavonone) is present in very small amount, for impregnation on flamboyán wood of a 0.02-percent solution repelled attack for 154 days, and the sample treated with 0.05-percent was not attacked in nearly 4 years.

From the sample of chlorophorin sent to Erdtman, extracted by F. E. King of Nottingham University, England, from *Chlorophora excelsa* Benth. & Hook f., an African tree commercially called iroko, a fraction was forwarded for tests with *Cryptotermes brevis*. When used to submerge flamboyán wood, the 0.2-percent-solution sample resisted attack for 234 days, and the 0.5-percent block remained uneaten over 3 years later.

Tectoquinone ( $\beta$ -methylantraquinone) from East Indian teak, *Tectona grandis* L., has the best record, for the length of time during which the impregnated wood has resisted attack, the 0.5-percent-solution impregnation having been attacked after 536 days, but the 1-percent, despite repeated tests, remained unharmed 9 years after impregnation.

Most of the extractives which M. L. Wolf from obtained from Osage orange, *Machura pomifera* (Raf.) Schneider, were available in such small quantity that one could but report that they were not very effective in preventing termite attack at the greater dilutions. The principal one, pomiferin, could be supplied in sufficient amount so that a 1-percent solution was tested. The 0.5-percent-solution impregnation on flamboyán was eaten in a little over a year, but the 1-percent continued to resist termite attack for 880 days, or approximately  $2\frac{1}{2}$  years. One other extractive which Wolf from calls "substance I," for which no structural formula has been proposed, but of which the molecular formula is  $C_{23}H_{24}O_6$ , is much more resistant to termite attack than is pomiferin. It is bright yellow in color and stains flamboyán so intensely that termites eating the 0.05-percent-solution impregnation after 236 days had abdomens bright with the purplish comminuted wood particles in process of digestion. When impregnated at greater concentrations the termites avoided the samples for over 2 years, and "substance I" may be more largely responsible for Osage orange being resistant to termite attack than the more obvious

pomiferin. Of the other extractives, pomiferin trimethyl ether at a 0.2-percent wood impregnation was not eaten for 112 days; isopomiferin dimethyl ether at 0.1-percent resisted attack for 225; tetra-hydro-osajin at 0.2-percent prevented termite attack for 707, but in every case the sample submitted by Wolfrom was so small that these data represent the end of the test with that particular extractive and give no realistic picture of what might be shown at the greater concentrations.

Some of the more repellent to termite attack of the chemicals submitted by the Laurel Hill laboratories were parachlorometa xylenol, flamboyán samples impregnated with 0.5-percent solution finally being attacked 277 days later;  $\alpha$ -phenyl-4-hydroxy-cinnamic acid after 319; resorcinol acetone after 354; chlorinated phenol potassium acetaldehyde sulfonate after 319 days, and when the 2-percent solution was used, in just a year; 2,4-chlorophenol monochlor potassium acetaldehyde disulfonate after 523 days; the 1-percent in 561 days, and the 2-percent after 2½ years; butyl 4-chlorobenzoyl acrylate at 0.5-percent after 661 days; ortho-dichloro-benzene-fumaryl-chloride, of which the 0.2-percent impregnation was eaten in 47 days, but the 0.5-percent impregnation was not eaten in over 2½ years; hexachlorocyclopentadiene dimer, of which the 0.2-percent impregnation was eaten in 166 days, but the 0.5-percent sample remained uneaten after 5 years; dibenzoyl ethylene, of which the 0.2-percent resisted attack for 341 days, and the 0.5-percent impregnation was not eaten 2½ years later; phenol heptachlor-propane, of which the 0.02-percent impregnation resisted attack for 667 days, the 0.2-percent for 675, and the 0.5-percent was not attacked in a little over 2 years; oxygenated hexachlor-cyclopentadiene dimer, of which the 0.2-percent impregnation resisted attack for 675 days, and the 0.5-percent was not attacked in 5 years; quinone-cycloactatetraene which imparted resistance for over 2 years at a 0.05-percent impregnation, but at 0.5-percent was eaten in 988 days.

Xanthone (Laurel Hill) was but slightly repellent to termite attack in diluted applications, the sample treated with 0.2 percent being eaten in 67 days, but at 0.5 percent the treated flamboyán wood resisted attack for 1,053 days, and the 1-percent sample was not attacked after nearly 7 years. In the hope that some combinations of xanthone might be even more resistant, a tetrachlorxanthone was something of a disappointment, with the 0.5-percent-solution impregnation eaten in 468 days, the 1-percent in 592 and the 2-percent in 594. But the 2-methoxy and the 4-methoxy at a 0.2-percent concentration prevented attack for 182 to 200 days, and the 0.5-percent impregnations were not eaten after 6 years.

Of the variants of the basic DDT formula, Laurel Hill submitted 1, 1-diphenyl (4-hydroxy-3,5-dichlor) 2,2,2-trichlorethane, of which the 0.5-percent impregnation prevented attack for 454 days and the 1-percent

for 514. The 1,1-di(4-hydroxy-2,5-dichlorophenyl) 2,2,2-trichlorethane at 0.5 percent was not eaten for 615 days, and the 1-percent impregnation remained uneaten 5 years afterward. As an extreme indication of how long a test must be conducted before one can be at all sure of the result, 1,1-di(2-hydroxy-3,5-dichlorophenyl) 2,2,2-trichlorethane is an outstanding example, for the impregnations using 0.05-percent solutions were eventually eaten over 5 years after impregnation, and the 0.1 percent only 3 days later, with the results on exposure of the 0.2 percent to termites as yet uncertain, presumably awaiting another 5 years of test. Thus one must consider with caution 1,1-di(4-hydroxy-2-methyl-5-isopropyl) 2,2,2-trichlor-ethane, of which the 0.05-percent impregnation was eaten in 38 days, but the 0.1-percent resisted attack almost 2 years later; and 1,1-di(4-hydroxy-2-methyl-5-chlorophenyl) 2,2,2-trichlorethane, of which samples impregnated with the 0.005-percent solution was eaten in 19 days, at a 0.01-percent impregnation remained resistant for over 1½ years.

The Q-137 of Rohm & Hass, 1,1-bis (*p*-ethylphenyl)-2,2-dichlorethane, impregnated on flamboyán wood at 0.5 percent prevented attack for over 2 years, but has been available for test for such a short additional time that no prediction can be made with any assurance as to its permanence at greater concentrations. The same is true of Prentox Strobane, originally produced by Prentiss Drug & Chemical Co., now transferred to B. F. Goodrich Chemical Co., of which the 0.02-percent impregnation prevented termite attack for 711 days.

Diazinon, originally synthesized by H. Gysin in the laboratories of J. R. Geigy S. A., Basle, Switzerland, with the formula O,O-diethyl-O-(2-isopropyl-4-methyl-pyrimidyl-6) thionphosphate, was made experimentally available in the United States by the Geigy Co. Inc., late in 1952. The flamboyán wooden block impregnated with a 0.1-percent solution was attacked just 2 years after treatment. It is too early to judge what its eventual value may be.

#### UNDESIRABILITY OF TOXICITY

The fundamental distinction between ordinary insecticides and chemicals being tested for permanence in immunizing wood to termite attack is that the former are toxic and the latter preferably nontoxic, for toxicity to termites of any chemical will presumably make it temporary in its repellent properties. Thus the metallic dimethyl-dithiocarbamates produced by du Pont primarily as fungicides, but which, incidentally, are toxic to termites at great dilutions when impregnated on wood samples, eventually lose this toxicity and thus demonstrate that their repellent property is temporary. In less than 2 years after impregnation at 0.1 percent both the copper and zinc compounds were no longer toxic on samples of flamboyán



wood, and no longer protected it against attack. Ferric dimethyl-dithiocarbamate, or "Fermate", was also originally toxic, but 3 years after impregnation the wood samples impregnated with a 0.5-percent solution were eaten. The *p*-chlorophenyl *p*-chlorobenzene sulfonate of Dow is also initially toxic, but a year after impregnation at 0.05-percent the wood sample was attacked, and in 455 days even the 1-percent sample was eaten. Four years elapsed before the sample impregnated at 2 percent could be attacked by the termites, and even then the form of attack was deep tunnels into the interior of the sample, rather than superficial gouges on its face.

When the chemists of the Hercules Powder Co. were perfecting the insecticide "Toxaphene", one of the experimental samples submitted for test with termites was a crude 60-percent chlorinated terpene which was initially toxic, but of which impregnations at the 0.01-percent level could be attacked with impunity by the termites in 71, the 0.1-percent in 296, and the 1-percent in 484 days. This should not be interpreted as being equivalent to the residual effect of toxaphene applied as an insecticide, for all the applications of chemicals in the tests with termites were of submersion 10 minutes in a solution, which is quite different from superficial spraying of an emulsion, or a suspension in water.

Wood of the Trinidad and South American shrub, *Ryania speciosa* Vahl., placed in test with other woods in a petri dish, not only repelled the termites but within a few days killed all of them, even though they ate none of the wood. Its extractive, Ryania or Ryanodine, originally developed by Merck and later taken over by S. B. Penick & Co., and made commercially available as an insecticide, is correspondingly powerful. The chemists have not yet determined the chemical composition of Ryanodine. The sample of the undiluted commercial preparation when used at a 0.02-percent level to impregnant flamboyán was eventually attacked in 204 days, although at first it has been too toxic for test. The wood sample impregnated with 0.05 percent of Ryania was eaten slightly at a later period, but remained substantially repellent 5 years after impregnation, one noteworthy example of a chemical initially toxic which continued to be repellent.

The sample impregnated with commercially available and widely used water-soluble sodium pentachlorophenate (Monsanto), at the dilution at which Ryania resisted attack for 5 years at the 0.05-percent level, was eaten in 38 days, but at 10 times this concentration (0.5-percent) it withstood attack for nearly 10 years. Impregnation of wood with zinc pentachlorophenate at the 0.5-percent level was eaten in 650 days, and no sample with a greater concentration had been prepared for test. Actually none seems required, for copper pentachlorophenate, of which the impregnation at the 0.1-percent level was attacked in 111 days, withstood termites at 0.2 percent for over 9 years. In our experience no difficulty has been experienced in obtaining

perfect solutions at tropical temperatures, but it must be admitted that, although articles impregnated with copper pentachlorophenate are not stained and give no apparent indication of having been treated, a sprayed basket in which green bananas are brought from the market bears numerous purplish-brown spots where the juice oozed from the freshly cut stems.

Among the chemicals which enabled wood to withstand termite attack for long periods, triphenyl phosphate at a 0.5-percent level conferred protection on the flamboyán sample for 533 days; 3,4,3',4'-tetramethoxydibenzyl at 1 percent for 4 years; the zinc lake (acetic acid) of alizarin at 0.5 percent for 512 days; and the zinc lake (acetic acid) of anthrarufin and chrysazin, attacked at 0.2 percent in 96 days, resisted attack at 0.5 percent for 8 years. The adduct of abietic acid and maleic anhydride which Erdtman thought might show promise, has been under test only 2 years, but at the end of this period the 0.5-percent impregnation had been eaten by the termites.

Because the 0.1-percent impregnation of dimethyl-tetrachlor-phthalate of the Whitmarsh Research Laboratories of Penn Salt had resisted termite attack for nearly 3 years, it seemed possible that other combinations might be even more valuable. As it happened, however, the 0.1-percent concentration was eaten in 1,226 days, the 0.2-percent in 1,228, and the 0.5-percent was attacked 5 years after the original impregnation. Thus it is hardly surprising that the *n*-propyl of the 2,3,4,5-tetrachlorophthalate at a 0.5-percent level of impregnation was eaten in 623 days; a glycol (alkyd) resin at 0.5 percent in 643; a glycerol (alkyd) resin at 0.5 percent in 645; and a di-2-ethylhexyl at 0.2 percent in 659 days. The 0.5-percent-impregnated wood has not yet been attacked after a little more than 2 years in the test. The sample impregnated with 2,3,4,5-tetrachlor benzoic acid at a 0.02-percent level was eaten in 54 days, but there is as yet no report on the 0.05-percent dilution.

A miticide of Naugatuck Chemical Co., called "Aramite," imparted resistance to termite attack to wood for over 4½ years when used at a 0.5-percent concentration, but we have no report on the 1-percent impregnation.

Mallinckrodt's pyridyl mercuric stearate showed a remarkably even resistance to termite attack: The impregnation at a 0.1-percent level was attacked in 19; the 0.2-percent in 440; the 0.5-percent in 1,241 days; the 1-percent impregnation remained uneaten for 9 years. In all the other compounds of mercury this element has been only a unstable point of weakness, but Mallinckrodt's pyridyl mercuric chloride protected the wood sample when impregnated with a 0.2-percent solution for 9 years before it was attacked.

Because Commercial Solvents' "Dilan" has not been commercially or

experimentally available for so long a time, one can only report that the propane fraction of 2-nitro-1,1-bis (*p*-chlorphenyl), at a 0.5-percent level of impregnation protected the sample of flamboyán wood, for 4½ years, and at 0.2-percent the butane fraction did the same.

The first sample furnished by du Pont of their methoxychlor, 2,2-bis (*p*-methoxyphenyl) 1,1,1-trichlorethane, late in 1949, is still an effective preventive of termite attack at an impregnation of the 0.05-percent concentration on flamboyán wood. A subsequent sample consisting of 90 percent of (*p,p*-methoxyphenyl) and 10 percent of (*o*-methoxyphenyl), proved less effective, the 0.1-percent impregnation being attacked in 351 days.

Five years ago Nuodex Products submitted a sample of their Nuodex 72 for test. Flamboyán wood impregnated with a 0.05-percent solution of Nuodex 72 was eaten in 10 days; the 0.1-percent in 34 days; but for the subsequent 5 years the sample impregnated with the 0.2-percent solution of this coconutamine salt of tetrachlorphenol resisted termite attack. At the same time a sample of Nuodex 136 was submitted; flamboyán wood impregnated therewith at a 0.1-percent level was eaten in 9 days, but the 0.2-percent sample remained immune to termite attack for nearly 6 years. The manufacture and sale of this chemical, zinc petroleum sulfonate, has been taken over by the Cellu-san Division, Dalworth Inc., Simsbury, Conn. Both of these chemicals are not only available commercially, but had been formulated for commercial impregnation of wood to protect against fungi and bacteria before their value against termites was recognized.

Nearly 6 years ago, when the chemicals synthesized by Julius Hyman still bore only his code numbers, and Aldrin was 118 and Dieldrin 497, small samples were made available for test through the courtesy of Mortimer D. Leonard, a former employee of the Station. These were intended for use against white grubs, in the control of which Aldrin proved very effective, but a small part of the experimental samples was used for the impregnation of flamboyán wood. From the very start these chemicals proved very repellent, the samples impregnated with 0.02-percent Aldrin not being eaten until 289 days had elapsed, and with 0.02-percent of Dieldrin, 201 days. Wood samples impregnated with the 0.5-percent solution were not attacked for nearly 3 years, those at 1 percent remained immune. The record of these particular chemicals is not so remarkable, however, as that of Hyman 49-RL-268, now called Isodrin, and Hyman 49-RL-269, now called Endrin, which, like the gamma isomer of BHC, as compared with the other isomers, differ in only one characteristic from Aldrin and Dieldrin, yet show a remarkable difference in the permanence with which they repel termite attack. The flamboyán sample impregnated with a 0.02-percent solution of

Endrin was eaten in 752 days, and at 0.05-percent remained entirely resistant to attack for nearly 5 years; the sample impregnated with 0.02 percent of Isodrin was eaten in 758 days; at 0.05 percent it was immune to termite injury 5 years later.

Aldrin is 1,2,3,4,10,10-hexachlor-1,4,4 $\alpha$ ,5,8,8 $\alpha$ -hexahydro-1,4-endo, exo-5,8-dimethanonaphthalene; Isodrin is 1,2,3,4,10,10-hexachlor-1,4,4 $\alpha$ ,5,8,8 $\alpha$ -hexahydro-1,4-endo, endo-5,8-dimethanonaphthalene; Dieldrin is 1,2,3,4,10,10-hexachloro-6-7-epoxy-1,4,4 $\alpha$ ,5,6,7,8,8 $\alpha$ -octahydro-1,4-endo, exo-5,8-dimethanonaphthalene; Endrin is 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4 $\alpha$ ,5,6,7,8,8 $\alpha$ -octahydro-1,4-endo, endo-5,8-dimethanonaphthalene.

#### DISCUSSION

The large number of compounds tested which had less than the value of pentachlorophenol in their permanence of resistance to termite attack have been cited only for the record. As far as dry-wood termites are concerned, they are valueless. The exception of citing DDT is made only because of publicity given to that chemical for other insecticidal purposes. Indeed, it is only for the record that the chemicals merely "as good as" pentachlorophenol are mentioned at all, for, unless they are competitive on a price basis, they can hardly be recommended in preference that well-known and widely tested chemical. In the same way, those chemicals which are merely "as good as" sodium pentachlorophenate and copper pentachlorophenate are noted primarily for the record. But those chemicals, some of which are only experimentally available, which for the longer periods of test are clearly more effective in dry-wood termite control, are certainly worthy of earnest consideration by any insecticide manufacturer. Even those which have been tested only a short time merit consideration, especially if they can be synthesized at low cost when produced on a commercial scale. Indeed, these most effective chemicals may actually prove to be the cheapest on a price basis, costing less than the solvent in which they are dissolved. Of the compounds of which only the date on which they were eaten is reported, this is within such a short time before the date of correction of proof that it may be considered the *known* length of time that the next greater concentration has resisted attack. Whether the sample with the next greater concentration will be eaten within a few days, weeks, months, years, or never, cannot be predicted, and should not be assumed on the basis of supposed similarity to some other chemical.

#### RESISTANT AT 2-PERCENT IMPREGNATION

*DDT*: 1-percent impregnated on almácigo wood attacked in 38 days; 2-percent uneaten in 10.5 years.

## RESISTANT AT 1-PERCENT IMPREGNATION

- Pentachlorophenol* (Monsanto): 0.5-percent-solution impregnated on almá-cigo wood attacked in 273 days; 1-percent slightly eaten in 337 days, not subsequently eaten in 11 years.
- Pyridyl mercuric stearate* (Mallinckrodt): 0.5-percent eaten in 1,241 days; 1-percent uneaten after 9 years.
- Tectoquinone* ( $\beta$ -methylantraquinone): 0.5-percent eaten in 536 days; 1-percent uneaten after 9 years.
- Zinc lake* (acetic acid) of  $\beta$ -chlorantraquinone: 0.5-percent eaten in 96 days; 1-percent uneaten after 6 years.
- Zinc lake* (acetic acid) of quinizarin: 0.5-percent eaten in 96 days; 1-percent uneaten after 6 years.
- Diphenyl mercury*: 0.5-percent eaten in 176 days; 1-percent uneaten after 8.5 years.
- Piperonyl cyclohexenone* (Dodge & Olcott): 0.5-percent eaten in 219 days; 1-percent uneaten after 7 years.
- 4,6-Dinitro-o-sec-butylphenyl* (Dow): 0.5-percent eaten in 244 days; 1-percent uneaten after 7 years.
- Xanthone* (Laurel Hill): 0.5-percent eaten in 1,053 days; 1-percent uneaten after 6.5 years.
- Genecide acids* (Laurel Hill): 0.5-percent eaten in 163 days; 1-percent uneaten after 6.5 years.
- Dimethyl tetrachlorphthalate* (Penn Salt): 0.5-percent eaten in 5 years; 1-percent uneaten after 6 years.
- Dinitro-o-phenyl phenol*: 0.5-percent eaten in 69 days; 1-percent uneaten after 6 years.
- 4-Iodox xanthone* (Laurel Hill): 0.5-percent eaten in 124 days; 1-percent uneaten after 6 years.
- Cupric salt of 3-penylsalicylic acid* (Dow: K-4738): 0.5-percent eaten in 79 days; 1-percent uneaten after 6 years.
- 2,4-Dichlorphenyl-2-phenyl benzoate* (Laurel Hill): 0.5-percent eaten in 126 days; 1-percent uneaten after 6 years.
- Dihydropinosylvin monomethyl ether* (Erdtman): 0.5-percent eaten in 1,279 days; 1-percent uneaten after over 5 years.
- $\beta$ -Chlorethyl- $\beta$ -(*p*-tert-butyl phenoxy)  $\beta$ -methyl ethyl sulfite, "Aramite" (Naugatuck): 0.5-percent eaten in 1,632 days; 1-percent uneaten after 5 years.
- 1,1-Di(4-hydroxy-2,5-dichlorphenyl) 2,2,2-trichlorethane* (Laurel Hill): 0.5-percent eaten in 615 days; 1-percent uneaten after nearly 5 years.
- Aldrin* (Hyman 118) Shell: 0.5-percent eaten in 1,230 days; 1-percent uneaten after nearly 6 years.
- Dieldrin* (Hyman 497) Shell: 0.5-percent eaten in 1,230 days; 1-percent uneaten after nearly 6 years.

## RESISTANT AT 0.5-PERCENT IMPREGNATION

- Sodium pentachlorophenate* (Monsanto): 0.2-percent eaten in 746 days; 0.5-percent uneaten after 8 years.
- 2-Methyl xanthone* (Laurel Hill): 0.2-percent eaten in 200 days; 0.5-percent uneaten after 6 years.
- 4-Methyl xanthone* (Laurel Hill): 0.2-percent eaten in 182 days; 0.5-percent uneaten after 6 years.
- Zinc lake* (acetic acid) of *Anthrarufin and Chrysazin*: 0.2-percent eaten in 96 days; 0.5-percent uneaten after 8 years.
- Ammonium dinitro-ortho-sec-butylphenol*: 0.2-percent eaten in 59 days; 0.5-percent uneaten after 6 years.
- 1,1-Di(2-hydroxy-3,5-dichlorophenyl) 2,2,2-trichlorethane* (Laurel Hill): 0.2-percent eaten in 1,895 days; 0.5-percent uneaten after over 5 years.
- Hexachlorcyclopentadiene dimer* (Laurel Hill): 0.2-percent eaten in 166 days; 0.5-percent uneaten after 5 years.
- Oxygenated hexachlorcyclopentadiene dimer* (Laurel Hill): 0.2-percent eaten in 675 days; 0.5-percent uneaten after 5 years.
- 2-Nitro-1,1-bis(p-chlorophenyl)propane* (Commercial Solvents): 0.2-percent eaten in 240 days; 0.5-percent uneaten in over 5 years.
- Chlorophorin* (King of Nottingham U.): 0.2-percent eaten in 234 days; 0.5-percent uneaten after 4 years.
- Pinosylvin dimethyl ether* (Erdtman): 0.2-percent eaten in 577 days; 0.5-percent uneaten after 3 years.
- Ortho-di-chlorobenzene fumaril chloride* (Laurel Hill): 0.2-percent eaten in 47 days; 0.5-percent uneaten after nearly 3 years.
- 2,4,2',4'-Tetranitrostilbene* (Erdtman): 0.2-percent eaten in 2 years, 4 months.
- Dibenzoyl ethylene* (Laurel Hill): 0.2-percent eaten in 341 days; 0.5-percent uneaten after 2.5 years.
- Di-2-ethylhexyl-2,3,4,5-tetrachlorphthalate* (Penn Salt): 0.2-percent eaten in 659 days; 0.5-percent uneaten after 2 years.
- Glycol (alkyd) resin 2,3,4,5-tetrachlorphthalate* (Penn. Salt): 0.2-percent eaten in 69 days; 0.5-percent uneaten after 2 years.
- Phenol heptachlor propane* (Laurel Hill): 0.2-percent eaten in 675 days; 0.5-percent uneaten after 2 years.
- 1,1-Bis(p-ethylphenyl) 2,2-dichlorethane* (Rohm & Haas Q-137): 0.2-percent eaten in 652 days; 0.5-percent uneaten after over 2 years.
- Coconutamine salt of tetrachlorphenol* (Nuodex 72) Nuodex Products: 0.1-percent eaten in 34 days; 0.2-percent eaten in 5 years, 4 months.
- Zinc petroleum sulfonate* (Nuodex 136) "Cellu-san" Darworth Inc.: 0.1-percent eaten in 9 days; 0.2-percent eaten in 5 years, 10 months.

## RESISTANT AT 0.2-PERCENT IMPREGNATION

- Copper pentachlorophenate* (Monsanto): 0.1-percent eaten in 11 days; 0.2-percent uneaten after 9 years.
- Pyridyl mercuric chloride* (Mallinckrodt): 0.1-percent eaten in 27 days; 0.2-percent uneaten after 9 years.
- 2-Nitro-1,1-bis (p-chlorophenyl) butane* (Commercial Solvents): 0.1-percent eaten in 335 days; 0.2-percent uneaten after 4.5 years.
- Vulpinic (lichen) acid* (Erdtman): 0.1-percent eaten in 159 days; 0.2-percent uneaten after 3 years.
- Azobenzene* (Erdtman): 0.2-percent eaten in 3 years, 2 months.
- 2,4-Dichlorstilbene* (Erdtman): 0.1-percent eaten in 277 days; 0.2-percent uneaten after 2.5 years.
- 0,0-Diethyl-0-(2-isopropyl-4-methyl-pyrimidyl-6) thionphosphate "Diazinon"* (Geigy): 0.1-percent eaten in in 2 years.

## RESISTANT AT 0.1-PERCENT IMPREGNATION

- 1,1-Di(4-hydroxy-2-methyl-5-isopropyl) 2,2,2-trichlorethane* (Laurel Hill): 0.05-percent eaten in 38 days; 0.1-percent uneaten in less than 2 years.

## RESISTANT AT 0.05-PERCENT IMPREGNATION

- Methoxychlor 1949* (du Pont); *2,2-bis(p-methoxyphenyl)1,1,1-trichlorethane*: 0.02-percent eaten in 1 year; 0.05-percent uneaten after 5 years.
- Isodrin: 1,2,3,4,10,10-hexachlor-1,4,4a,5,8,8a-hexahydro-1,4-endo, endo-5,8-dimethanonaphthalene* (Hyman 49-RL-268): Shell: 0.02-percent eaten in 758 days; 0.05-percent uneaten after nearly 5 years.
- Endrin: 1,2,3,4,10,10-hexachlor-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo, endo-5,8-dimethanonaphthalene* (Hyman 49-RL-269) Shell: 0.02-percent eaten in 752 days; 0.05-percent uneaten in nearly 5 years.
- Prentox "Strobane"* (B. F. Goodrich): 0.01-percent eaten in 564 days; 0.02-percent eaten in less than 2 years.
- Ryanodine*: (originally Merck, now S. B. Penick): 0.02-percent eaten in 204 days; 0.05-percent slightly eaten after 5 years.
- Taxifolin* (Erdtman): 0.02-percent eaten in 154 days; 0.05-percent uneaten after 3.5 years.
- 2,3,4,5-Tetrachlorbenzoic acid* (Penn Salt): 0.02-percent eaten in 54 days; 0.05-percent uneaten in 2 years, 7 months.
- 2,4-Dihydroxyphenanthrene* (Erdtman): 0.05-percent eaten in 594 days.

## RESISTANT AT 0.01-PERCENT IMPREGNATION

*Pinosylvin monomethyl ether* (Erdtman): 0.005-percent untested; 0.01-percent uneaten after 4.5 years.

*1,1-Di(4-hydroxy-2-methyl-5-chlorophenyl)2,2,2-trichlorethane* (Laurel Hill): 0.005-percent eaten in 19 days; 0.01-percent uneaten in 2 years, 3 months.

*2,4-Dihydroxybenzalaniline* (Erdtman): 0.002-percent eaten in 257 days; 0.005-percent eaten in 3 years, 2 months.

## RESISTANT AT 0.005-PERCENT IMPREGNATION

*2,4-Dinitro-2',4'-dichlorstilbene* (Erdtman): 0.002-percent untested; 0.005-percent uneaten after 4.5 years.

*4,4'-Dinitrostilbene* (Erdtman): 0.005-percent uneaten after 4.5 years.

## SUMMARY

The high resistance to decay and insect attack of some woods which makes them of such great value for building and the construction of furniture for use in the Tropics, is due to the presence in the heartwood of each species of a comparatively minute amount of some unique chemical. Such chemicals appear to have little or no survival value for the tree itself, and indeed often result in its early elimination by selective cutting in virgin tropical forests. The less desirable woods, however, may be given at least superficial protection by painting, spraying, submergence, or pressure-impregnation with such extracted constituents of resistant woods, or with other chemicals synthesized in the laboratory.

If not leached out by water, the protection afforded by such water-soluble chemicals as copper sulfate or zinc chloride and most repellent inorganic chemicals is permanent, but that resulting from surface impregnation of organic chemicals, because of their inherent volatility or instability, is often only temporary. Thus permanent effectiveness is of even greater importance than the concentration of the chemical used for wood impregnation, and for the present summarization is barely mentioned, unless for a greater period than 5 years, with full realization that even 5 years is far from being the equivalent of forever.

In preventing attack on such termite-susceptible woods as almácigo and flamboyán by the West Indian dry-wood termite, *Cryptotermes brevis* Walker, submergence for 10 minutes in a 2-percent solution of DDT has been effective twice for over 5 years.

A 1-percent solution of commercial pentachlorophenol impregnated into the wood has protected almácigo for 11 years; and for somewhat shorter periods so did the teak extractive tectoquinone; the zinc lakes (acetic



acid) of quinizarin and of  $\beta$ -chloranthaquinone; piperonyl cyclohexenone (Dodge & Olcott); 4,6-dinitro-*o*-sec-butylphenyl (Dow); dinitro-*o*-phenyl phenol (Dow); xanthone, 4-iodox xanthone, and genicide acids; 2,4-dichlorophenyl-2-phenyl benzoate (Laurel Hill); dimethyl tetrachlorophthalate (Penn Salt); Dow's K-4738; a cupric acid salt of 3-phenyl-salicylic acid; dihydropinosylvin monomethyl ether (Erdtman); Naugatuck's miticide "Aramite," and Shell's Aldrin and Dieldrin.

An impregnation of one-half of 1 percent of sodium pentachlorophenate (Monsanto) has protected almácigo wood against termite attack for 8 years, as did also that of the zinc lake (acetic acid) of anthrarufin and chrysazin. Similar protection for 5 to 6 years was afforded flamboyán wood by ammonium dinitro-ortho-sec-butylphenol, or "Sintox", of Standard Agricultural Chemicals. The following experimental chemicals synthesized at the Laurel Hill Laboratories: 2-methyl and 4-methyl xanthone, hexachlorocyclopentadiene dimer and its oxygenated dimer, and 1,1-di(2-hydroxy-3,5-dichlorophenyl)2,2,2-trichlorethane, did the same. Two Nuodex Products: cocountamine salt of tetrachlorophenol (Nuodex 72) and zinc petroleum sulfonate (Nuodex 136), now renamed "Cellu-san", have done likewise for over 5 years on flamboyán.

An impregnation of one-fifth of 1 percent of copper pentachlorophenate (Monsanto) has protected almácigo wood against termite attack for 9 years.

An impregnation of one-twentieth of 1 percent of 1949 Methoxychlor (duPont), 2,2-bis(*p*-methoxyphenyl)1,1,1-trichlorethane, has protected flamboyán against termite attack for 5 years, as did also Isodrin and Endrin (Shell) synthesized by Julius Hyman, and the extractive of *Ryania speciosa*, Ryanodine (Ryania of Merck, now of S. B. Penick).

Of the extractive pinosylvin monomethyl ether from *Pinus sylvestris*, the impregnation on flamboyán of one-hundredth of 1 percent has not been attacked by termites in 4.5 years. Of the other experimental chemicals synthesized in the Laboratory of Organic Chemistry, the Royal Institute of Technology, Stockholm, Sweden, the two-hundredth of 1-percent impregnation of 2,4-dihydroxybenzaliline resisted termite attack for 3 years, 2 months before being eaten, while at this extreme dilution, 4,4'-dinitrostilbene and 2,4-dinitro-2',4'-dichlorostilbene are still immune from termite attack 4.5 years after impregnation.

#### RESUMEN

La alta resistencia a los ataques de los insectos y a podrirse de cada madera, propiedades necesarias para darle valor como material de construcción y para la manufactura de muebles en los trópicos, se deben a la presencia de comparativamente pequeñas cantidades de alguna substancia química específica para cada especie de árbol. Estos agentes químicos aparentemente tienen muy poco valor, o quizás ninguno, en lo que se refiere a

la supervivencia del árbol en sí, y casi siempre los arboles desaparecen pronto durante el corte selectivo en los bosques vírgenes tropicales. A las maderas menos deseables, sin embargo, podrían dárseles, por lo menos protección superficial, pintándolas, asperjándolas, sumergiéndolas o impregnándolas a presión con los constitutivos extraídos de las maderas resistentes, o con otros compuestos químicos sintetizados en el laboratorio.

A menos que no se lave con el agua, la protección adquirida por medio de estos compuestos inorgánicos específicos, es permanente. No resulta así la protección que adquieren las maderas por medio de la impregnación superficial con agentes químicos orgánicos, ya que la volatilidad inherente o su inestabilidad es frecuentemente temporera. Por este motivo, la *permanencia* de la eficacia del agente químico es aún de mayor importancia que el grado de *concentración* del compuesto que se use para impregnar la madera. Claro está, que la eficiencia del tratamiento debe durar por mucho más tiempo que 5 años para poder considerarla recomendable. Se apunta aquí que cuando se sumergieron el almácigo y el flamboyán, maderas muy susceptibles a los ataques de la polilla de la madera seca, *Cryptotermes brevis* Walker, por 10 minutos en una solución al 2 por ciento de DDT, los efectos preservativos duraron por 10 años.

El pentaclorofenol comercial, a una concentración del 1 por ciento ha protegido la madera de almácigo por 11 años después de impregnada; por otros períodos más cortos, la madera de almácigo ha sido protegida por los siguientes agentes químicos: extractivo tectoquinona de teca; piperonil cyclohexenona (Dodge & Olcott); 4,6-dinitro-*o*-sec-butilfenol (Dow); pigmentos de zinc (ácido acético) de quinizarina y de beta-clorantaquinona; dinitro-*o*-fenilfenol (Dow); xantona, 4-iodo-xantona, y los ácidos genticicos 2,5-dichlorofenil-2-fenolbenzoato (Laurel Hill); dimetyl tetracloroptalato (Penn Salt); K-4738 de Dow; sal cúprica del ácido 3-fenolsalicílico; éter dihidropinosilvino monometílico (Erdtman); miticido "Aramite" de Nau-gatuck; y Aldrín y Dieldrín de Shell.

Una impregnación de medio por ciento de pentaclorofenato de sodio (Monsanto) ha protegido la madera de almácigo contra la polilla por 8 años, al igual que con una de pigmento de zinc (ácido acético) de antrarufín y crysazín. La madera de flamboyán fué protegida, de 5 a 6 años, cuando se impregnó con el dinitro-orto-sec-butilfenol de amoníaco, conocido por "Sintox W" de la "Standard Agricultural Chemicals" y con los agentes químicos sintetizados por los laboratorios "Laurel Hill", a saber: 2-metilo y 4-metilo xantona; dímero de hexaclorociclo pentadieno y su dímero oxigenado; y 1,1-di (2-hidroxi-3-5-diclorifenil) 2,2-tricloretano.

Pudo protegerse la madera de almácigo de los ataques de la polilla por 9 años cuando se impregnó con una solución que tenía una quinta parte de un por ciento de pentaclorofenato de cobre (Monsanto).

La madera de flamboyán se logró proteger por 5 años impregnándola con dos productos "Nuodex"; la sal coconutamina de tetraclorofenol (Nuodex 72) y el petróleo sulfonato de zinc (Nuodex 136), ahora llamado "Cellusan".

En el 1949, la madera de flamboyán impregnada con  $\frac{1}{20}$  de un por ciento de metoxyclor (Dupont), 2,2-bis (p-metoxifenil) 1,1,1,-tricloroetano, conservó su resistencia por 5 años. Igual pasó cuando se impregnó con Iso-drín y Endrín (Shell), ambos productos sintetizados por el Dr. Julius Hyman, y con el extractivo de *Ryania speciosa*; ryanodina ("Ryania" Merck, ahora de S. B. Penick).

El extractivo de *Pinus sylvestris*, éter monometilo de pinosilvino de los compuestos químicos 2',4',2',4',-tetranitrostilbeno, sintetizados por los laboratorios del Dr. Erdtman en Suecia, cuando se usaron para impregnar la madera de flamboyán, a razón de  $\frac{1}{100}$  de un por ciento, esta resistió los ataques de la polilla por  $4\frac{1}{2}$  años. La misma madera impregnada con los compuestos 2,4-dinitro-2',4'-diclorostilbeno y 4,4'-dinitrostilbeno, a razón de  $\frac{1}{200}$  de un por ciento ha resistido hasta ahora por  $4\frac{1}{2}$  años.

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