

PERSISTENCE STUDIES OF INSECTICIDES: II DEGRADATION OF GARDONA[®] ON
WHITE PINE LEADERS (PINUS STROBUS L.) AFTER AERIAL APPLICATION FOR
CONTROL OF WHITE PINE WEEVIL (PISSODES STROBI PECK) IN ONTARIO, 1973

By

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Information Report CC-X-62

Forestry Service
Environment Canada

February, 1974

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INTRODUCTION

The white pine weevil (Pissodes strobi Peck) is the most serious insect pest of eastern white pine (Pinus strobus L.) in North America. Weevil attack causes considerable reduction in quality and quantity of merchantable lumber (Brace 1971) thereby producing significant economic loss (Marty 1959). During the past two decades, weevil damage was substantially reduced by the aerial application of various chlorinated insecticides such as DDT (Connola et al 1955, Crosby 1958, Connola 1961, Kirby et al 1962, Connola and Smith 1964, Godwin and Reeks 1967), lindane (Crosby 1958, Hastings and Risley 1962) and methoxychlor (Howse and Sippel 1969, 1970; DeBoo and Campbell 1971, 1972; Sundaram et al 1972, Sutherland and DeBoo 1973, Sundaram 1973b) to infested pine stands in early spring when the adult weevil activity is high. Current restrictions on the use of the persistent chlorinated hydrocarbons have brought about an increased dependence on various organophosphorus insecticides. A wide range of chemicals of this class (dialkyl aryl phosphates and phosphorthioates) has been tested (Nigam 1972) in the laboratory against white pine weevil by the Chemical Control Research Institute (C.C.R.I.) in an attempt to seek a safe, effective substitute for the organochlorines. Among them, Gardona *[®] [2-chloro-1-(2, 4, 5-trichlorophenyl)-vinyl dimethyl phosphate] (previously known as SD 8447) showed promise. The insecticide was field tested by C.C.R.I. in April 1973 by aerielly applying a water-based formulation of Gardona on a

* Shell Registered Trade Name.

white pine plantation near Sault Ste. Marie in Ontario. This report describes the results of experiments conducted during that spray operation. The objectives of the study were:

- (i) To develop analytical methods for the determination of Gardona[®] in white pine leaders,
- (ii) to study its persistence and possible fate in the leader samples and
- (iii) to evaluate critically the overall efficacy of the toxicant in weevil control.

MATERIALS AND METHODS

Experimental Plan

Experimental study of aerial application of Gardona[®] for control of white pine weevil was conducted at the Kirkwood Forest Management Unit north of Thessalon, Ontario. The plantation selected for the spray program was located in the township of Rose. A 60-acre spray block designated as R2, with white pine content of approximately 50% of the standing trees, was chosen for the spray study. An untreated check area of 80 acre plantation (R5) separated from the treated plot (R2) by approximately 5 miles served as the control.

Gardona Application

Gardona[®] wettable powder (75% WP) was supplied by Shell Canada Ltd., Toronto. The spray material was prepared by mixing thoroughly

appropriate amount of the insecticide in water to give 1 lb active ingredient (A.I.)/acre in 2 gal. (U.S.) of water to which 0.08 gal. of Target E[®] (molasses) was added as adjuvant. The resulting formulation was sprayed on April 30, 1973 at 1930 hrs using a Stearman aircraft fitted with 4 Micronair AU2000 emission units at the rate of 1.0 lb. A.I./acre. The gas-liquid chromatographic (GLC) analysis of the technical material and the spray mixture* showed that the insecticide used was of 84% purity.

Sampling Plan

Leader samples for residue analysis were taken from both the untreated and treated blocks immediately before treatment (prespray), 1 hr after (0 day), then 1, 4, 9, 15, 20, 26, 35 and 50 days later. Each sample consisted of 10 nearly uniform subsamples (leaders) taken at random throughout each plot. Samples were stored in polythene bags in a cooler at 0° F and transported immediately to the C.C.R.I. laboratory in Ottawa for analysis.

Analytical Procedure

No gas chromatographic method has been reported in the literature for estimating Gardona[®] residues from white pine leaders. After a number of trial experiments (Table I) using spiked leader samples, a sensitive analytical method was developed based on the

* GLC analysis was done 36 hrs after the preparation of spray mixture.

method developed by Shell Company *. The method involved solvent extraction, partitioning, cleanup by liquid-solid column chromatography, elution, concentration under low pressure and GLC estimation by using suitable columns and a flame photometric dectector. The procedure used is briefly described below and schematically illustrated in Fig. 1.

Extraction Method

Prior to extraction each sample was thawed, cut into small pieces using a hand clipper and chopped in a Hobart grinder ¹. Each sample was then mixed by hand to ensure even distribution of the sub-samples. An aliquot (10g) was taken for moisture determination (AOAC 1955). A 20 g ground leader sample was weighed and placed in a Sorvall Omini-Mixer ² container with 100 ml of acetonitrile ³. The mixture was blended at high speed for 5 min. and the leader matrix was filtered under suction through a Buchner funnel using Whatman # 1 paper. Glass-wool plug was also found to be equally effective. The filtrate flashed to about 30 ml and was transferred quantitatively to a 1 l separatory funnel which contained 600 ml of distilled water, 10 ml of 5% Na₂SO₄ (aq) and 100 ml of hexane ⁴. The mixture was shaken vigorously for 30 sec.,

* Shell Development Company, Biological Sciences Research Center, Modesto, California, Anal. Method MMS-R-231-1, March, 1970.

1 Hobart Mfg. Co., Toronto, Food Cutter Model # 84142.

2 Ivan Sorvall Inc., Norwalk, Conn., U.S.A.

3 Residue-free solvents distilled in glass by: Caledon Laboratories Inc., 53 Armstrong Ave., Georgetown, Ont.

4 Residue free solvent, distilled in glass by Caledon Laboratories.

the solvents allowed to layer, and the lower aqueous phase was further extracted twice with 100 ml of hexane. The aqueous phase was then discarded. The combined hexane phase (ca 300 ml) was washed with 100 ml of water, the washings were added to the aqueous phase and the hexane layer was dried by passing through a column of anhydrous sodium sulphate ¹ (100 g), flash evaporated ² to a small volume (10 ml) and submitted to column cleanup. Fortified check leader samples yielded 90% recoveries (See Table I) with the extraction procedure just outlined.

Cleanup Procedure

Twenty grams of 4:1 deactivated Florisil ³ containing 8% water-celite ⁴ sandwiched between 10 g of anhydrous Na₂SO₄ ⁵ was poured into Shell design chromatograph column ⁶ (length 260 mm, ID 20 mm) fitted with fritted glass disc and Teflon stopcock at one end and 300 ml glass reservoir at the other. The contents of the column were packed uniformly using an automatic mixer ⁷. The column was prewetted with

-
- 1 Fisher S-420
 - 2 Flash evaporator, Buchler Instruments, 1327 Sixteenth St. Fort Lee, N.J., 07024, U.S.A.
 - 3 Fisher F-100, 60-100 mesh
 - 4 Fisher C-212, Celite 545
 - 5 Fisher S-421, anhydrous powder
 - 6 Expertise Glass, Montreal, P.Q.
 - 7 Deluxe Mixer (#S8220), Scientific Products, Evanston, Ill., U.S.A.

25% diethyl ether ¹ in hexane and adjusted to 2-3 drops/sec. The column was not allowed to run dry. As soon as the liquid reached the top of the adsorbent bed, the stopcock was closed and the concentrated leader extract (ca 10 ml) was transferred quantitatively to the column. The column was eluted with 300 ml of 25% ether in hexane ². The eluate was light yellow (See Table I) and flashed to 2 ml for GLC analysis.

Gas Chromatography

A Hewlett-Packard ³ (H-P) 7610A gas chromatograph fitted with a Tracor flame photometric detector containing phosphorus interference filter (mu 526), a 1-mv H-P strip chart recorder (model 71284) and a 4-ft x 0.25-in., OD U-shaped glass column packed with 5% OV 1 on chromosorb W (60/80 mesh, AW-DMCS) were used. The oven, inlet and detector temperatures were 190, 210, 170° C, respectively. The nitrogen carrier gas was of high purity with inlet pressure of 50 psi and gas flow of 60 cc/min. The flow of hydrogen, oxygen and air were 150, 20, 50 cc/min respectively. Range setting was 10³, and attenuation was 32. With these parameters, the retention time for Gardona was 10.1 min.

1 Fisher, E-193, spectroanalyzed

2 The moisture content of the adsorbent was found to be critical and determined the volume of the eluate used. High moisture content (>8%) required low volume of ether-hexane mixture.

3 Hewlett-Packard, Route 41, Avondale PA 19311, U.S.A.

Standard curve for Gardona [®] was prepared at frequent intervals during sample analyses by plotting peak heights vs insecticide mass in ng. Two or four μ l aliquots of the extract were injected into the chromatograph and from the measurement of resultant peak heights, the insecticide concentration was computed from the appropriate calibration curve.

Typical chromatograms of the insecticide standard and fortified leader samples after cleanup are shown in Figs. 6 and 7.

TABLE I
Studies on Recovery and Column Chromatographic Cleanup
of Gardona[®] from White Pine Leaders*

Extraction Solvents	Column Cleanup	Elution Solvents	Recovery (%)	Comments
** "				
IPA: Hexane (1:1)	Florisil (0 % H ₂ O)	Ether:Hexane (1:3) 300 ml	10	Light yellow solution, no GLC interference, poor recovery
"	" (5 % H ₂ O)	"	45	"
"	" (8 % H ₂ O)	"	80	Yellow solution; reasonable GLC interference satisfactory recovery.
"	" (10 % H ₂ O)	"	85	Deep yellow solution; appreciable background in GLC; good recovery
"	" (8 % H ₂ O)	Benzene:Hexane (1:4) 300 ml	--	Deep yellow solution; very high GLC interference
"	Charcoal: Celite (6:4 g)	"	35	Yellow solution; poor recovery
"	"	Ether:Hexane (1:3) 300 ml	20	"
CH ₂ Cl ₂ :CH ₃ OH (1:1)	Florisil (8% H ₂ O)	"	70	Deep yellow solution; high GLC background; low recovery
CH Cl ₃ :CH ₃ OH (9:1)	"	"	--	Solution highly coloured and dirty
"	Charcoal: Celite (6:4g)	"	25	Light yellow solution, minimum GLC interference, poor recovery
"	"	15% Benzene in Hexane (300 ml)	50	Yellow solution, appreciable GLC interference poor recovery
Ethyl acetate	Florisil (8 % H ₂ O)	Ether:Hexane (1:3) 300 ml	70	Light yellow solution, minimum GLC background, low recovery

* 20 g of chopped leader samples were spiked with 2 µg of analytical grade Gardona[®] and extracted as described in the text. The extract was submitted to column cleanup after hexane-water partition. All solvents used were nonograde and glass distilled.

** IPA: Isopropyl alcohol.

TABLE I - Cont'd

Ethyl acetate	Charcoal: Celite (6:4 g)	15% Benzene in ethyl acetate	70	Yellow solution, appreciable GLC interference, low recovery
CH ₃ CN	Florisil (0 % H ₂ O)	Ether: Hexane 1:3; 300 ml	15	Light yellow solution, minimum GLC interference, poor recovery
"	" (5 % H ₂ O)	"	50	"
"	" (8 % H ₂ O)	"	90	Light yellow solution, minimum GLC interference, good recovery +
"	" (10% H ₂ O)	"	90	Deep yellow solution, appreciable GLC interference, good recovery.
"	Charcoal: Celite (6:4 g)	"	20	Light yellow solution, no GLC interference, poor recovery
"	"	15% Benzene in Hexane	25	Yellow solution, minimum GLC interference, poor recovery.
"	"	15% Benzene in Ethyl Acetate	25	"
"	"	25% Benzene in Hexane	--	Solution deep yellow and cloudy.

+ Analytical procedure described was developed on the basis of this experiment.

See Fig. 8 for extraction efficiency.

TABLE II
Recovery of Gardona®* from White Pine Leaders**

No. days Post-spray	Leader Mass (g)	Moisture Content (percent)	Gardona® Concn. (wet mass) (ppm) +	Residual Gardona® (wet mass) (percent) +	Gardona® Concn. (dry mass) (ppm)	Residual Gardona® (wet mass) (percent)
Pre-spray	20	58	N.D.	0	N.D.	0
0	20	57	4.20	100	9.76	100
1	20	56	3.60	86	8.18	84
4	20	55	2.08	50	4.62	47
9	20	60	1.18	28	2.95	30
15	20	58	0.60	14	1.43	15
20	20	57	0.30	7.1	0.70	7.1
26	20	59	0.28	6.6	0.68	7.0
35	20	62	0.18	4.2	0.47	4.8
50	20	61	0.17	4.1	0.44	4.5

* Average of two experiments.

** Control samples from Plot R5 gave negative results for Gardona® on all post-spray days.

+ Results used in the present discussion.

N.D. Not detected.

TABLE III
Efficacy of Gardona[®] and Methoxychlor Treatments by Aircraft^{*} for Control of
White Pine Weevil in the Kirkwood Forest Management Unit, 1973^{**}

Treatment	Acres Treated (Acres)	Leader injury for White Pine Weevil									Percent reduction in leader injury (between years)
		1972 (Pre-treatment)			1973 (Post-treatment)						
		No. of Trees Examined	No. of Trees Weeviled	Percent Weeviled	No. of Trees Examined	No. of Trees Weeviled	Percent Weeviled	0-day concn. (ppm)	50-day concn. (ppm)	t _{1/2} (days)	
Gardona [®] 1.0 lb A.I. in 2 gal water/acre + 0.08 gal. Target E (molasses).	60	1069	184	17.2	1098	82	7.5	4.20	0.17	5.0	56.4
Methoxychlor 2.5 A.I. in 1.75 gal. of fuel oil and xylene (4:3, v/v)/ acre.	100	2033	261	12.8	2126	56	2.6	12.82	0.21	5.0	79.7
Untreated Check (Control)	80	1074	174	16.2	1004	162	16.1	--	--	--	0

* Stearman aircraft, 4 micronairs AU2000

** DeBoo, R.F. 1973. Personal communication.

Insecticide concentrations are expressed in ppm "as sampled".

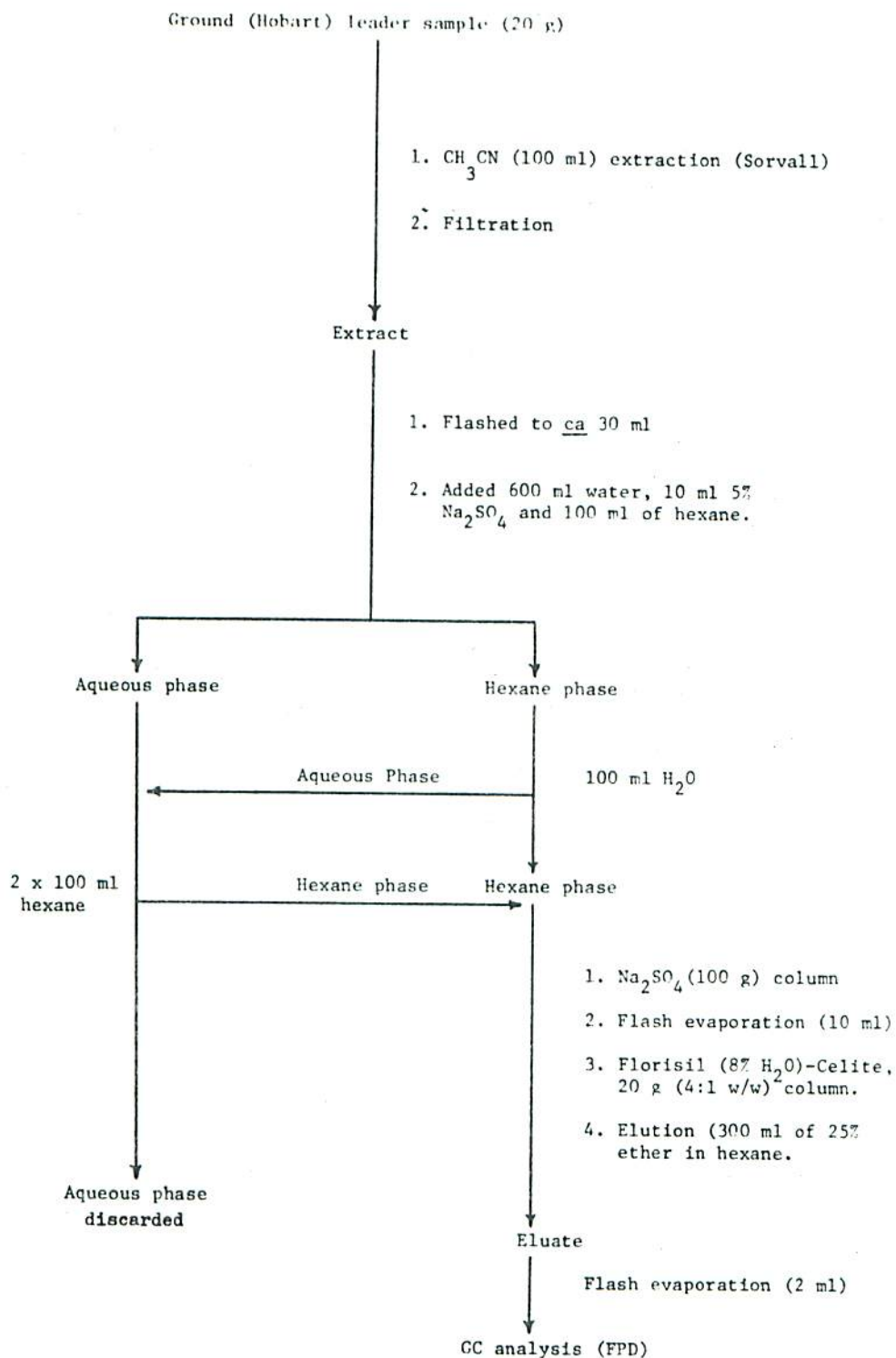


Fig. 1 Schematic representation of extraction and cleanup procedure for Gardona R in white pine leaders.

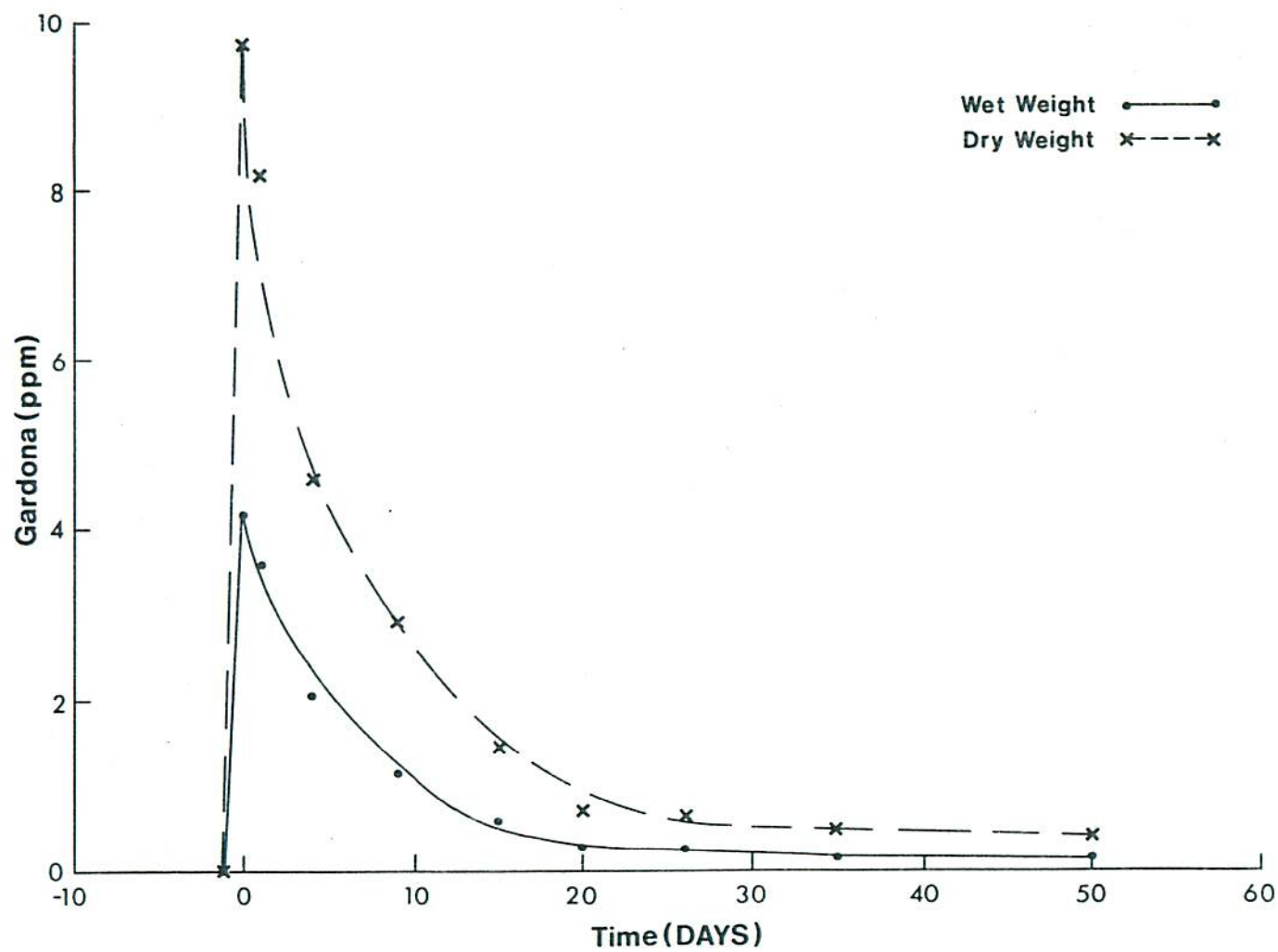


Fig. 2. Dissipation of Gardona [®] from white pine leaders.

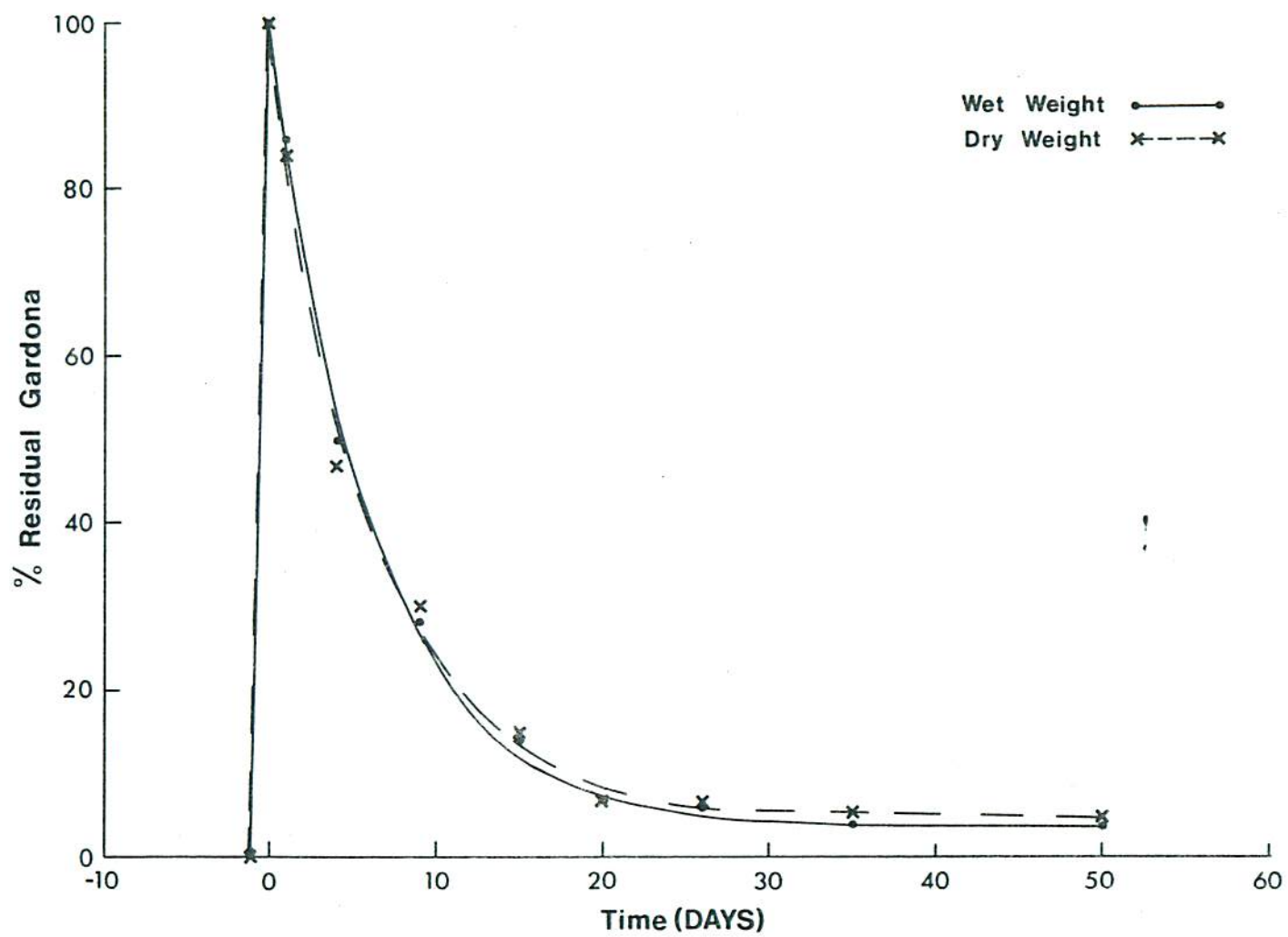


Fig. 3. Variation of percent residual Gardona ^(R) with time.

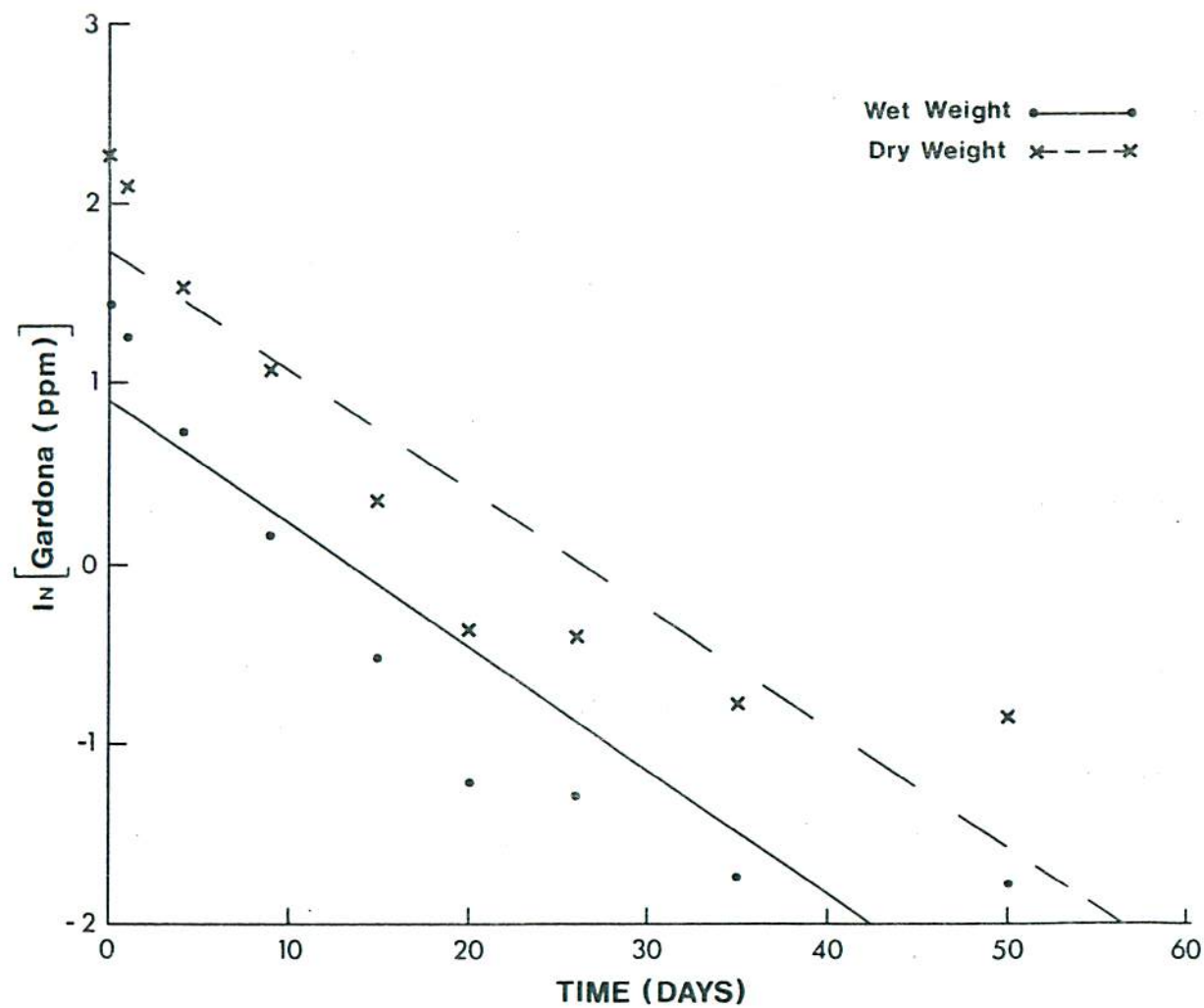


Fig. 4. Rate of variation of residual Gardona^(R) in white pine leaders
 Wet weight $Y = 0.910 - 0.021 X$, ($T_{1/2} = 10.04$ days)
 Dry weight $Y = 1.730 - 0.030 X$, ($T_{1/2} = 10.50$ days)

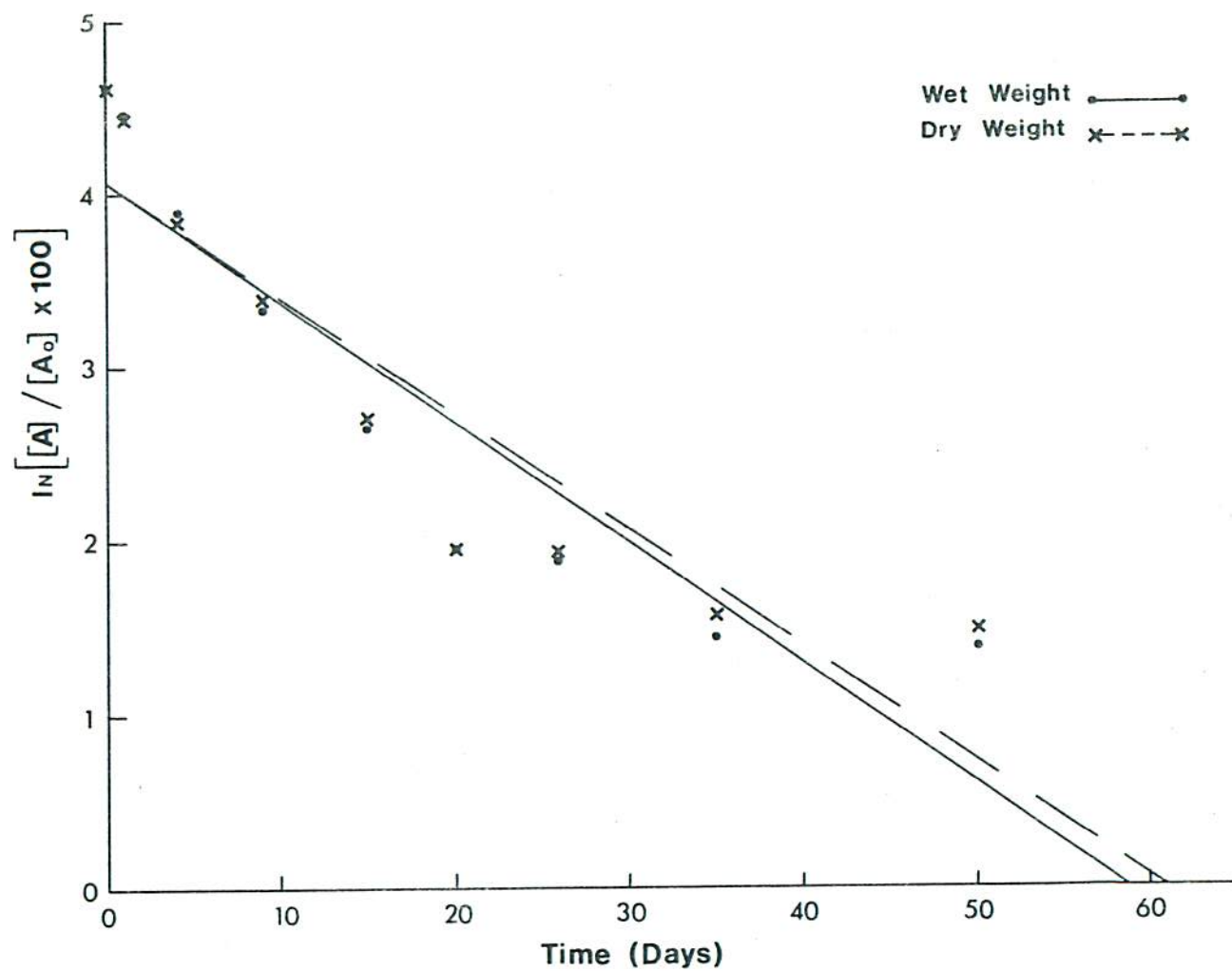


Fig. 5. Kinetics of the dissipation of Gardona[®] in white pine leaders
 Wet weight: $Y = 4.073 - 0.069 X$
 Dry weight: $Y = 4.064 - 0.066 X$

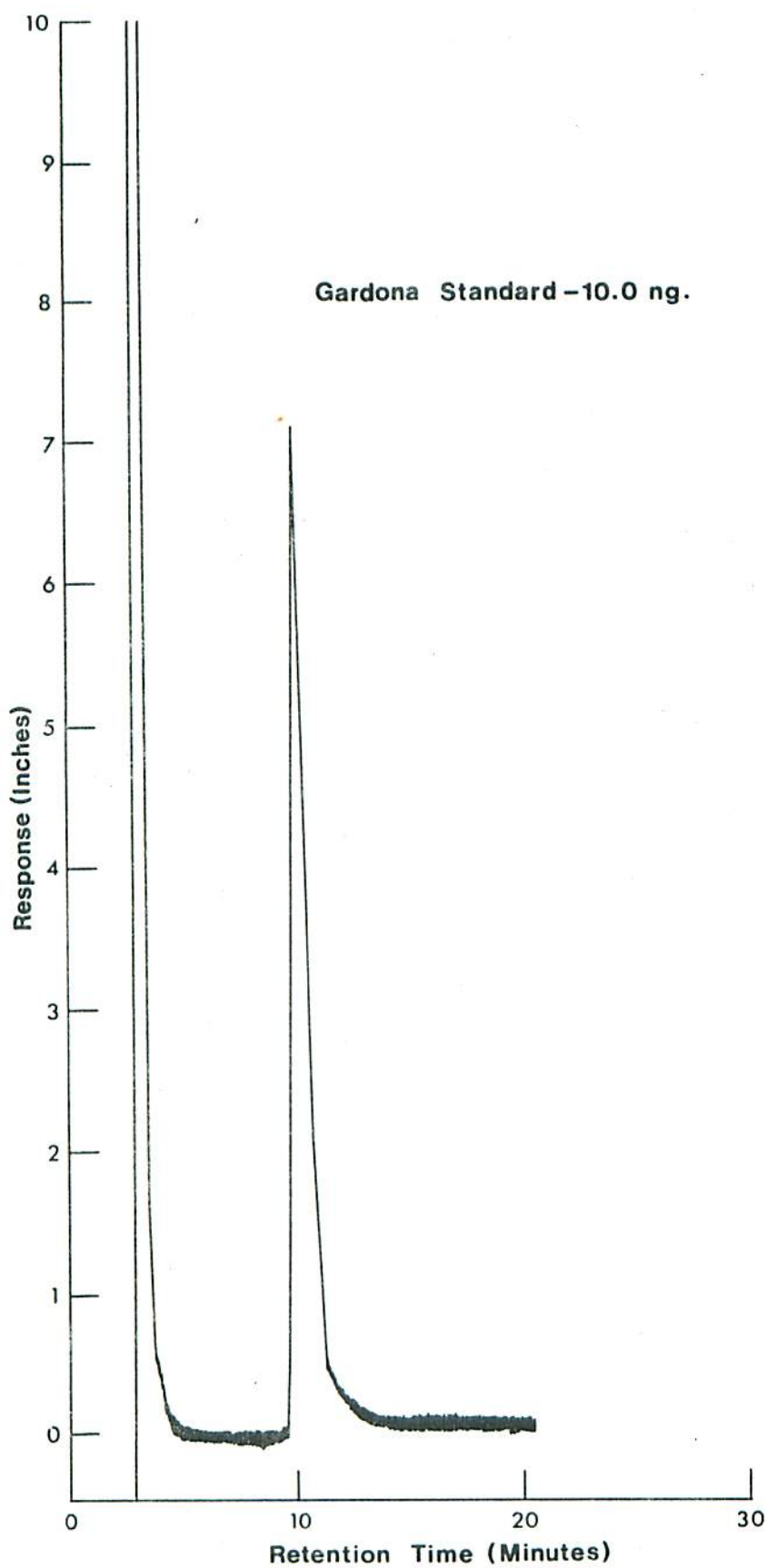


Fig. 6. Chromatogram of Gardona[®] standard

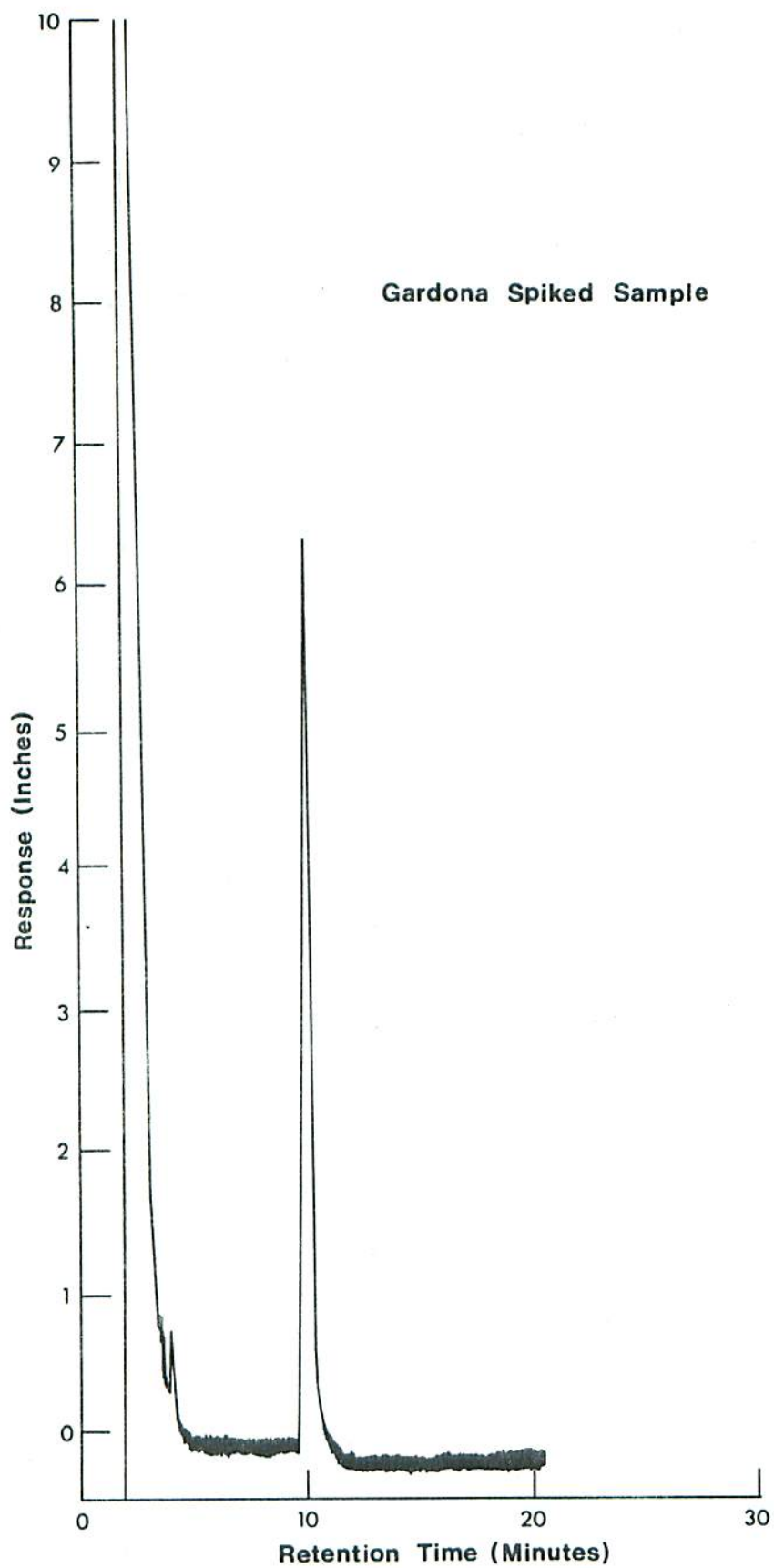


Fig. 7. Chromatogram of spiked leader with Gardona[®]

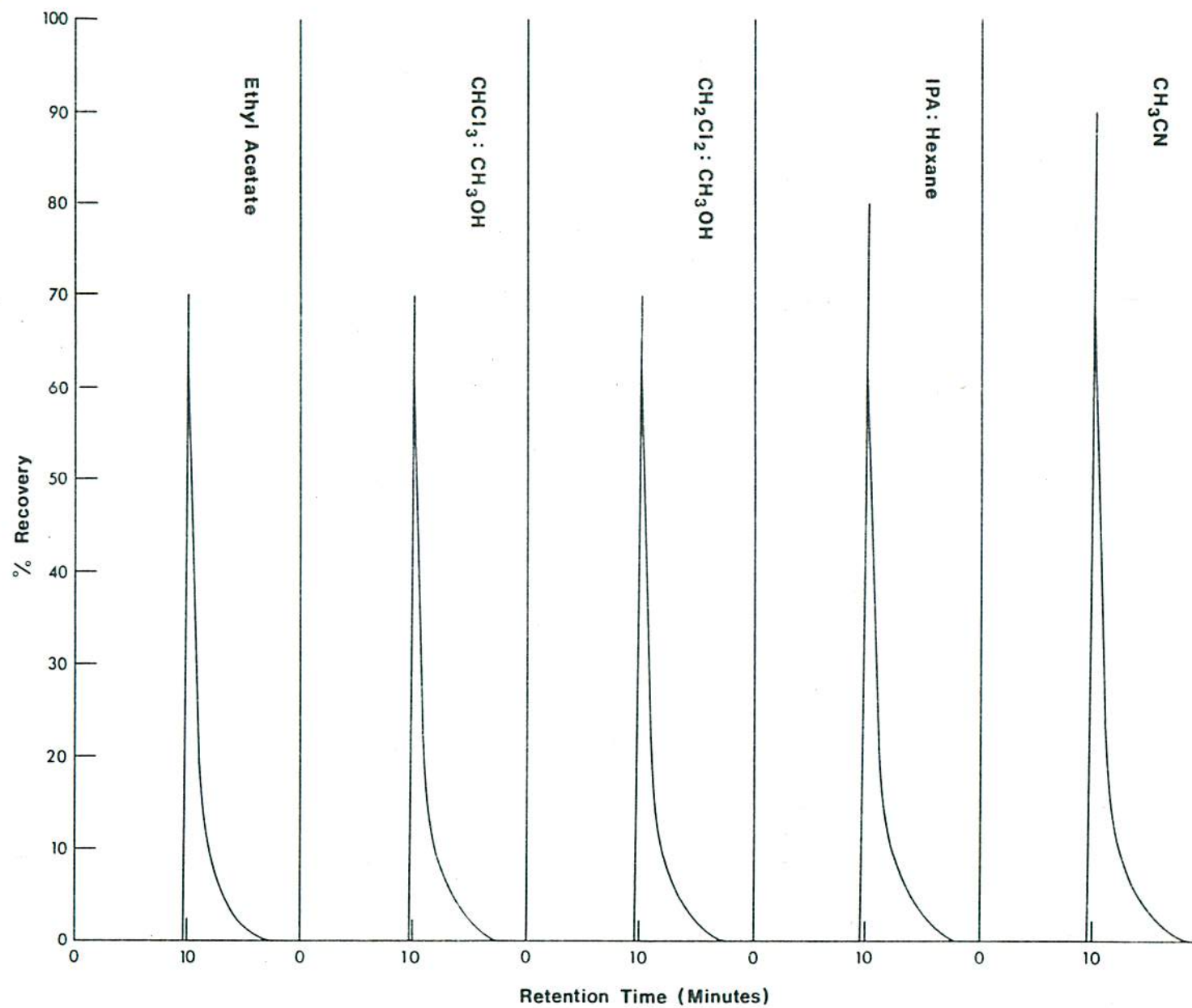


Fig. 8. Extraction efficiency of Gardona ^(R) from spiked leaders using different solvents.

RESULTS AND DISCUSSION

Analytical Methodology for Gardona[®]

Table I shows the various experiments conducted on the recovery and cleanup of Gardona[®] from spiked white pine leaders. Extraction of the insecticide from the substrate with various solvents and solvent mixtures showed that acetonitrile was superior to others in extraction efficiency with minimum co-extractives. Ethyl acetate and chloroform-methanol, solvents very commonly used for the extraction of fenitrothion from spruce and fir foliage (Yule and Duffy 1972), and IPA (isopropanol)-hexane recommended by Shell Company (loc. cit.) and methylene chloride-methanol used by Sundaram et al (1972) for extracting methoxychlor were found to be unsatisfactory (See Fig. 8) for Gardona[®].

The cleanup procedure involved hexane partition and column chromatography on deactivated Florisil - Celite adsorbent mixture. The water content of the adsorbent was found to be a critical factor in the cleanup procedure. If the Florisil used had a low moisture content (< 8%), the insecticide was not released from the adsorbent matrix or if it had high moisture content (> 8%) the insecticide and the associated impurities were readily eluted, causing appreciable background interference in GC analysis.

The column eluant used also had considerable influence on desorbing the insecticide molecules from Florisil. Threehundred ml of ether-hexane (1:3 v/v) solvent mixture was found to be sufficient to eluate Gardona[®] from the column. Solvent mixtures containing benzene were found to be unsatisfactory (Table I), primarily due to the high

dissolution power of the aromatic hydrocarbon to interfering impurities adsorbed on the column matrix.

Gardona[®] molecule contains both Cl and P, so it can be analysed by EC (sensitive to Cl) and FPD (sensitive to P) detection. Spiked samples were analysed by EC detection; the response was not satisfactory (hence not recorded in this report) due to background interference requiring further cleanup and low range of linearity observed. On the other hand, FPD analyses were found to be superior without having any of those difficulties. The 5% OV1 on Chromosorb W column was found to be equally efficient compared to the columns used by Shell researchers (loc. cit.). Typical chromatograms obtained with this column are shown in Figs. 6 and 7.

The analytical method described here for Gardona from white pine leaders, and schematically represented in Fig. 1, gave > 90% recovery of the insecticide. The method developed is believed to be applicable with some modifications, to other substrates like foliage, tissues, soil, etc.

Persistence of Gardona[®] Insecticide in Leaders

The amount of Gardona[®] found in white pine leaders from pre-spray and post-spray samples are shown in Table II. Each residue value is the average of at least two determinations and variation between replicates was generally within 12 percent. Prespray and control samples did not contain any insecticide. From the results it is evident that the initial decrease in concentration was rapid. The maximum insecticide content found was 4.20 ppm (as sampled) on zero day but 50% of it

was lost within 4 days. After 9 days only 28% remained (1.18 ppm) which declined gradually to 4.1% (0.17 ppm, wet mass) on the last day of sampling (50 day). A plot of insecticide concentration vs time (days) (Fig. 2) and percent residual Gardona[®] vs time (Fig. 3) for wet and oven dry leaders showed an exponential but rapid decrease of residue levels. After 35 days the rate of decrease was extremely small, a decrease of only 0.01 ppm (0.1%) in 15 days. The last sample collected 50 days after the spray contained only 0.17 ppm corresponding to 4.1% of the initial concentration. The slow disappearance of the insecticide from the leaders on the later part, after spray application, is probably due to the adsorption of the toxicant in the epicuticular waxes present on leader surfaces forming a homogenous solid solution which dissipated rather slowly by volatilization, weathering, chemical and enzymatic degradations. Similar low level residue concentrations of fenitrothion and methoxychlor were observed in spruce and fir foliage (Yule and Duffy 1972) and white pine leaders (Sundaram 1973).

Logarithmic plots of Gardona[®] concentration (ppm) and percent residual insecticide in as sampled (wet) and oven dry leaders are nearly linear (Figs. 4 and 5) and appeared to follow first-order kinetics (Sundaram et al 1972, Sundaram 1973). The chemical half-life of the insecticide i.e., the time taken to decrease from 4.20 to 2.10 ppm (wet mass) was found to be 5.0 days^{*} from Fig. 2. The value is low

* For oven dry samples the half-life was 4.8 days (see Fig. 2).

indicating that the compound was not persistent due to its low intrinsic stability and underwent chemical and biochemical degradations as well as dissipated from the substrate surface by volatilization.

Efficacy of Gardona[®] in Weevil Control

The efficacy of aerially sprayed Gardona[®] and methoxychlor for white pine weevil control is shown in Table III. The results obtained using methoxychlor is included here for comparative purposes so that a choice of a suitable toxicant for future spray operations could be made based on experimental data.

The results of the 1973 study show that the application of Gardona[®] at the rate of 1.0 lb A.I. in 2 gal. water/acre did not provide an effective level of weevil control. Only 56.4% reduction in leader injury was observed between the years 1972 and 1973, which is far below the acceptable level of 85% (DeBoo and Campbell 1972). The zero day concentration of the toxicant was found to be only 4.20 ppm with a low chemical half life of 5.0 days. The inferior control is possibly due to the low dosage of the chemical applied (1.0 A.I./acre), and the overall intrinsic instability of the insecticide. Probably a satisfactory level of protection against weevil infestation could have been obtained using a higher dosage (ca 2.0 to 3.0 lbs A.I./acre) of the toxicant.

It is known (Sundaram 1973) that in aqueous media, dialkyl and aryl phosphates and phosphorothioates are hydrolysed at both the alkyl-phosphate and aryl-phosphate bonds, and the degradation process is greatly influenced by pH and temperature. Similar observations

have been recorded by Faust and Suffet (1966). The aqueous formulation of the insecticide used being a dynamic system favouring degradation, it is very likely that the toxicant was not very effective in giving a high level of leader protection. The addition of a molasses adjuvant (Target E) to the aqueous formulation did not improve the spray efficacy either. Probably an oil based spray formulation of Gardona[®] would be more effective for weevil control than the one used in 1973. It is well known that suitable formulents strongly affect the efficacy of insecticides (Mingelgrin and Yaron 1973). DeBoo and Campbell (1972) found that oil based sprays of insecticides were approximately four times more effective than aqueous formulations in reducing weevil densities. It will be useful to carry out further experimental aerial applications of Gardona[®] at increased dosages (2.0 to 4.0 lb A.I./acre) using fuel oil as solvent if satisfactory protection of leaders are expected. Low mammalian toxicity (Whetstone et al 1966, Gardner-Hopkins and Forshaw, 1968, Jennings 1970), rapid rate of disappearance in foliage and soils (Beynon and Wright 1969), low half-life, etc., show that Gardona[®] is a safe insecticide which could be exploited usefully in plantation protection if more explorative research and experiments are conducted to study its efficacy rather critically.

Comparison of Gardona[®] and Methoxychlor Treatments in Weevil Control

Data in Table III show that between the two spray treatments, methoxychlor application was effective in reducing weevil population density to an acceptable level of 79.7%, 23.5% higher than that of

Gardona[®] application. Assuming similar weather conditions, temperature and humidity in the two sprayed areas within the Kirkwood Forest Management Unit plantations after treatment, the half-life for both the insecticides were found to be the same, i.e., 5.0 days. The residue concentrations after an interval of 50 days were low; 0.17 ppm for Gardona[®] and 0.21 ppm for methoxychlor. The observed difference was only 0.04 ppm which is negligibly small. Nigam (1972) has shown that Gardona[®] was 12.4 times more toxic than methoxychlor in causing 50% mortality to adult white pine weevils. In spite of the observed low potency under controlled laboratory experiments, methoxychlor spray in the field was found to be offering good protection (79.7%) for trees against weevil attack. This satisfactory level of protection may be attributed largely (i) to the high dosage (2.5 lb A.I./ac.) applied, (ii) the oil formulation used which gave effective deposition and uniform coverage of the insecticide on the target (leader), (iii) the chemical structure of the toxicant and finally (iv) the intrinsic stability of the insecticide. It has been observed (Sundaram 1973) that in aqueous formulations, the medium (water) interacts with the insecticide molecules if they have favourable electronic distribution, making them unstable. Various organophosphates including Gardona[®] have such reactive sites in the molecule to interact with water thereby affecting the stability of the toxicant. Probably an oil formulation of Gardona[®] at higher dosage i.e., more than 1.0 A.I./acre, would have given a satisfactory protection of leaders against weevil attack.

Conclusion

The experimental spray operations conducted at the Kirkwood FMU plantations indicated that methoxychlor appeared to be more suitable than Gardona® in weevil control, at least at the dosages evaluated. Relatively large dosage (2.5 lbs A.I./acre) was required to obtain optimum level (80% +) of protection. The long term effects and immediate hazards of the insecticide and its possible degradation products on the plantation ecosystem is still largely unknown. Further studies on the persistence of the residue, its ecological impact and the effects of its breakdown products, on ecosystem, are necessary for proper evaluation of the toxicant, as a useful insecticide and as a suitable replacement for DDT in plantation research.

The results of 1973 spray application of Gardona® for weevil control was not encouraging, additional experimentation is required to assess its usefulness. The efficacy of an insecticide depends to some extent, on the formulation used and the mode of application. As pointed out earlier, oil based formulations may be more useful for organophosphorus insecticides because of enhanced spray efficacy (low volatility, minimal drift, optimum droplet size, etc.) than emulsion preparations for weevil control. It is apparent, then, that sufficient emphasis be placed on formulation research and development to enhance the intrinsic toxic potency of insecticides that show promise in experimental spray operations. Aircraft fitted with Micronair systems are ideal for large forest spraying, and they require perfect or near ideal weather conditions for maximum efficiency.

The small droplets (50-100 μ) produced by the system evaporate very rapidly and are susceptible to drift. It is difficult to get the emitted droplets to the target, i.e., bark surfaces of primary leaders of pine trees which constitute only a small fraction of the three-dimensional aerial spray target relative to the pine tree canopy. Consequently less insecticide deposition will impinge on target leaders compared to the emitted amount. The insecticide droplets are usually intercepted by non-target vegetation, landed on forest floor and lost by drift and volatility. Probably an aircraft equipped with conventional boom and nozzle may give satisfactory weevil control because of larger and heavier droplets produced which will reach target leaders giving an even spray coverage. These are some of the unexplored areas in plantation research which warrant our immediate attention before looking into some alternative insecticides for weevil control.

SUMMARY

White pine trees (Pinus strobus L.) were sprayed experimentally with Gardona[®] mixed with an adjuvant (Target E) at the rate of 1.0 lb. A.I. in 2 gal. water/acre by aircraft. Leader samples were collected from sprayed trees at various time intervals for GLC assay. Homogenization of leaders and extraction by acetonitrile showed 90% recovery. The cleanup procedure involved hexane-water partitioning, concentration, and column chromatography on partially deactivated Florisil. The zero day deposit concentration

in leaders was 4.20 ppm which decreased rapidly at the beginning thereafter gradually to 0.17 ppm after 50 days. The dissipation rate of the insecticide was high with low persistence and residue half-life of 5.0 days. The reduction in weeviled trees was only 56.4% showing that Gardona[®] treatment did not provide sufficient protection to white pines against weevil attack compared to methoxychlor. Additional experimentations in formulation development and spray techniques are required to evaluate fully the usefulness of Gardona[®] in plantation weevil control.

ACKNOWLEDGEMENTS

The author is very much indebted to R.F. DeBoo of this Institute for arranging this collaborative study and for the provision of results recorded in Table III. He and L.M. Campbell kindly arranged to provide all the necessary leader samples from the Kirkwood Forest, north of Thessalon for the investigation. Sincere thanks are due to R.A. Brunette, Ontario Ministry of Natural Resources, Little Rapids, Ont., for the assistance rendered in sample collections.

Assistance of Shell Canada Ltd. in supplying analytical standards of Gardona[®] and Midair (Canada) Ltd. in spraying the insecticide is greatly appreciated.

Sincere thanks are due to P. Davis, W. O'Brien and G.G. Smith for providing the necessary technical assistance and carrying out the routine analytical work. The author acknowledges particularly the assistance of P. Davis in preparing this report.

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