The Relationship Between Structure and Fungicidal Activity of Pyridine Alkane and Carbinol Compounds as Turf Fungicides

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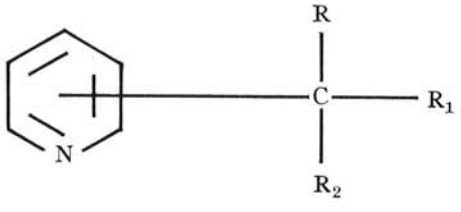
ABSTRACT

The fungicidal activity of a number of pyridine alkane and carbinol compounds related to α,α-diphenyl-3-pyridinemethanol was studied. Laboratory, greenhouse, and field experiments demonstrated control of several turf pathogens with cycloalkyl substitution on the carbinol carbon. Substitution on the 3 position of pyridine resulted in maximum activity against all pathogens tested. Another moiety on the pyridine ring in addition to an active substitution at the 3 position eliminated activity. Poor fungicidal activity resulted when the hydrogen or hydroxyl on the alpha carbon was replaced with chloro, amino, or methoxyl groups. No significant increase in activity resulted when substitutions were made on phenyls attached to the alpha carbon. The greatest increase in activity was noted when certain cycloaliphatic groups were substituted for one or both phenyl moieties on alpha carbon.

Determinations of ED_{50} and ED_{95} values for the most active cyclohexyl-pyridine compounds indicated that dosages required were considerably less than those for Daconil 2787 and Dyrene. Field studies indicated that dosages of the effective fungicides increased exponentially with the increase of time between applications in the control of *Sclerotinia homoeocarpa* on Astoria bentgrass (*Agrostis tenuis*). Phytopathology 60:771-778.

The unusual fungicidal activity of compounds in the 3-substituted pyridine alkane and carbinol series was discovered in our laboratories (4) and reported by Brown et al. (1), Thayer et al. (3), and Whaley et al. (5). This discovery led to the synthesis of a number of fungicidally active related pryidine compounds. These compounds containing one or more cycloalkyl substituents were efficacious against certain turf pathogens. The primary objective of the present study was to determine the chemical structure in the 3-substituted pyridine series exhibiting maximum fungicidal activity against selected turf pathogens, and to compare this activity with that of the 2- and 4-substituted pyridine alkanes and carbinols. In addition, ED_{50} and ED_{95} values were determined in greenhouse studies for the three cycloalkyl compounds most active against dollar spot incited by *Sclerotinia homoeocarpa* F. T. Bennett. Field studies were conducted to confirm results obtained on dollar spot in the greenhouse.

The general structural formula for the pyridine alkanes and carbinols discussed is represented by:



where R can be hydrogen, hydroxyl, methoxyl, chloro, cyano, or amino, and R_1 and R_2 are phenyl, chlorophenyl, isopropyl, cyclopropyl, cyclobutyl, or cyclohexyl groups.

MATERIALS AND METHODS.—*Dilution in agar studies.*—Five turf pathogens (*Helminthosporium sorokinianum* Sacc. ex Sorokin, *Sclerotinia homoeocarpa, Rhizoctonia solani* Kühn, *Fusarium roseum* f. sp. *cerealis* [Cke.] Snyd. & Hans., and *Pythium ultimum* Trow.) were chosen for the initial in vitro evaluation of all pyridine alkane and carbinol compounds.

The bioassay medium was prepared by dissolving 16 mg of the test compound in 0.5 ml dimethylsulfoxide (DMSO) and adding 249.5 ml tap water, resulting in a 64 ppm solution to which was added 12.5 g of Difco Czapek's agar. The medium was autoclaved for 20 min at 121 C and cooled, and 25-ml portions were poured into ten 90-mm petri dishes. Compounds in this series are not affected by autoclaving.

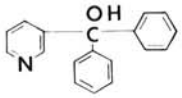
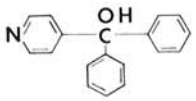
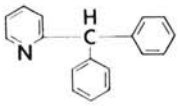
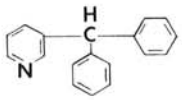
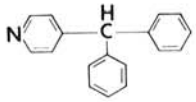
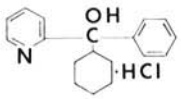
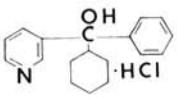
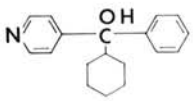
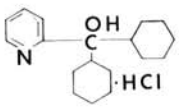
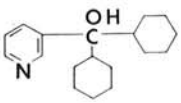
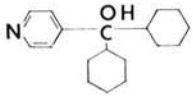
A 6-mm agar disc containing 7-day-old mycelium of the test fungus grown at 25 C was placed in the center of each dish containing the test compound and incubated under alternating light and dark conditions at 25 C for 72 hr. At this point, colonies of all five species on the untreated medium and DMSO controls had reached the outer edge of the petri dish. Colony diam measurements were taken and corrected for the 6-mm agar inoculum.

Greenhouse studies with Sclerotinia dollar spot and Rhizoctonia brown patch.—Inoculum was produced on vermiculite medium because the dry material could easily be sifted through the grass to the soil surface. A mixture containing 15% bran flakes, 1.0% dehydrated potato flakes, and 84% No. 3 vermiculite was saturated with a liquid containing 2.5 g NaCl, 2.0 g Difco yeast extract, 10.0 g glucose, 16.0 ml Difco nutrient broth, and 2.0 g N-Z Amine-Type A/liter of tap water. A 10-cm layer of this preparation was placed in a 40 × 30 × 20-cm stainless steel tray, covered with wrapping paper, and autoclaved for 30 min at 121 C. The tray was cooled to room temperature, inoculated with several agar discs containing mycelium, and incubated for 48-72 hr at 25 C. The infested vermiculite was spread in a shallow layer and allowed to dry for 48 hr at 25-30 C. This inoculum was viable for several months when stored at 5 C.

Plugs of turf, 11 cm in diam, were removed from an established Astoria bentgrass (*Agrostis tenuis* Sibth.)

nursery and placed in the greenhouse. Before using, the plugs were placed in pint plastic containers, watered, and trimmed to a height of 1 cm. They were then inoculated with either *Sclerotinia* or *Rhizoctonia* by spreading 5 ml of vermiculite inoculum over the surface and shaking the pot to assure that most of the particles had settled to the soil surface. The foliage was sprayed with a test compound or a 1.0% alcohol check through a DeVilbiss atomizing nozzle, and the pots were placed on a greenhouse cart, the bottom of which was

TABLE 1. Per cent control of five turf pathogens grown on Czapek's agar treated with 64 ppm of 2-, 3-, and 4-substituted pyridine alkane and carbinol compounds[a]

Fungicide		Fungi				
Structure	Name	*Helmintho-sporium sorokinianum*	*Rhizoctonia solani*	*Sclerotinia homoeocarpa*	*Fusarium roseum*	*Pythium ultimum*
		%	%	%	%	%
	α,α-Diphenyl-3-pyridinemethanol	100	0	100	100	0
	α,α-Diphenyl-4-pyridinemethanol	23	0	40	0	0
	2-(Diphenylmethyl) pyridine	65	67	100	56	0
	3-(Diphenylmethyl) pyridine	100	94	100	95	7
	4-(Diphenylmethyl) pyridine	65	0	100	65	69
	α-Cyclohexyl-α-phenyl-2-pyridinemethanol hydrochloride	56	69	71	37	0
	α-Cyclohexyl-α-phenyl-3-pyridinemethanol hydrochloride	100	100	100	71	100
	α-Cyclohexyl-α-phenyl-4-pyridinemethanol	26	33	65	0	96
	α,α-Dicyclohexyl-2-pyridinemethanol hydrochloride	62	82	69	38	96
	α,α-Dicyclohexyl-3-pyridinemethanol	50	100	100	100	100
	α,α-Dicyclohexyl-4-pyridinemethanol	14	25	39	7	46

[a] Per cent control based on growth of untreated checks (82 mm).

covered with a layer of water-saturated vermiculite. A tightly fitting lid was placed on the cart to assure a moisture-saturated atmosphere during the incubation period.

Fungicide application equal to 1.0 lb/acre was obtained by dissolving 1.15 mg of compound in 0.04 ml ethanol, diluting to 4.25 ml with tap water, and spraying on one 11-cm turf plug. This volume is equivalent to 10 gal/1,000 ft^2, which is within limits recommended for turf fungicide application in the field, and provided good wetting of the foliage in our studies.

Turf plugs inoculated with *Rhizoctonia* were incubated at 27 C, and those inoculated with *Sclerotinia* at 21-24 C. After incubation for 48-72 hr, the lids were removed from the cart moist chambers and readings made.

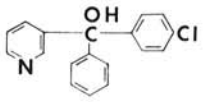
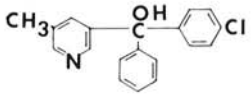
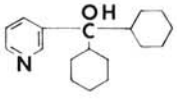
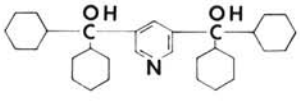
A completely random design was used for the in vivo greenhouse experiments. In each, treatments were coded and replicated three times. The disease rating scale used for all but the ED_{50} and ED_{95} determinations was based on a 1-5 rating system, indicating the percentage of area diseased (5 = no disease; 4 = 1-10%; 3 = 10-40%; 2 = 40-80%; 1 = 80-100% of area diseased). A modified Barratt-Horsfall disease rating system (2) was used in determining the per cent infection for plotting ED_{50} and ED_{95} values.

Field studies.—Sclerotinia dollar-spot field trials were conducted during the summer of 1966 in Greenfield, Indiana. A randomized block design with coded treatments was used to facilitate blind readings. Disease determinations were made on a weekly basis, using a modified Barratt-Horsfall rating system that permitted an estimation of the percentage of total area within each 15 ft^2 (4.57 m^2) plot with symptoms. On 8 June, approximately 1 month before the first treatment, all plots were inoculated with mycelium of the dollar spot pathogen. Treatments of 0.1-2.0 lb/acre were applied every 7, 14, or 21 days until 7 September. Spray volume was constant on all plots at 5 gal/1,000 ft^2 applied at 60 psi with all compounds formulated as 25% wettable powders.

RESULTS.—The in vitro evaluations indicate that certain groups attached to the 3 position of the pyridine give the widest spectrum of activity (Table 1). For example, α,α-diphenyl-3-pyridinemethanol completely inhibited the *Helminthosporium, Sclerotinia,* and *Fusarium* isolates; whereas α,α-diphenyl-4-pyridinemethanol only slightly inhibited *Helminthosporium* and *Sclerotinia.* Our *Rhizoctonia, Fusarium,* and *Pythium* isolates were not inhibited by the 4-substituted diphenylmethyl compound. This observation was further substantiated by three compounds in the methane series. At 64 ppm, 3-diphenylmethylpyridine caused inhibition of all pathogens except *Pythium.* The 4-substituted analogue permitted slight growth of *Helminthosporium, Fusarium,* and *Pythium,* but did not inhibit *Rhizoctonia.* The 2-substituted compound was slightly active against *Rhizoctonia,* but had no effect on *Pythium.* The phenylcyclohexyl and dicyclohexyl derivatives followed a similar pattern, in that the 3-substituted compound was clearly more active than when the same groups were placed in the 2 or 4 position of the pyridine ring.

In vivo greenhouse studies.—Compounds inhibiting 3 of the 5 organisms in the agar dilution test at 64 ppm were examined in in vivo tests using *Helminthosporium* leaf spot, *Sclerotinia* dollar spot, and *Rhizoctonia* brown patch. Fifty compounds met these criteria. These compounds were initially compared at 2 lb./acre with 2,4-dichloro-6-(*o*-chloroanilino)-*s*-triazine (Dyrene) and tetrachloroisophthalonitrile (Daconil 2787), two com-

TABLE 2. Disease control at 2.0 lb./acre of active ingredient of 3- and 3,5-substituted pyridine carbinol compounds against three turf diseases

Fungicide		Disease severity rating		
Structure	Name	*Helminthosporium* leaf spot	*Rhizoctonia* brown patch	*Sclerotinia* dollar spot
	α-(4-Chlorophenyl)-α-phenyl-3-pyridinemethanol	3[a]	5	5
	α-(4-Chlorophenyl)-5-methyl-α-phenyl-3-pyridinemethanol	4	3	2
	α,α-Bis(cyclohexyl)-3-pyridinemethanol	5	5	5
	3,5-Pyridine-bis(α,α-dicyclohexylmethanol)	1	1	1

[a] 5 = No disease; 4 = 1-10% leaf area diseased; 3 = 10-40%; 2 = 40-80%; 1 = 80-100%.

monly used commercial turf fungicides, at the recommended rate of 5 and 8 lb./acre of active ingredient, respectively.

Substitution on pyridine ring.—Substitution on another carbon atom of the pyridine ring, in addition to the 3 position, reduced fungitoxicity against *Rhizoctonia* and *Sclerotinia* (Table 2). The 3-substituted compound [α-(4-chlorophenyl)-α-phenyl-3-pyridinemethanol] gave excellent control of *Rhizoctonia* brown patch and *Sclerotinia* dollar spot at 2 lb./acre of active ingredient. When methyl was added to the 5 position of the pyridine, disease control was poor. One of the most active compounds, α,α-bis(cyclohexyl)-3-pyridinemethanol, controlled all three fungi at 1.0 lb./acre, but the addition of another α,α-dicyclohexylmethanol in the 5 position of the pyridine ring, to give 3,5-pyridine-bis(α,α-dicyclohexylmethanol), destroyed the efficacy of the fungicide on these three diseases.

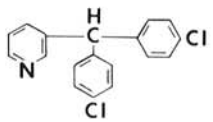
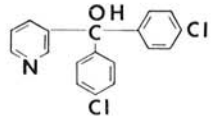
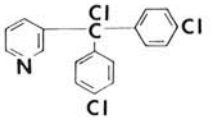
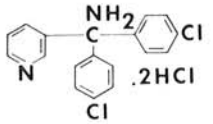
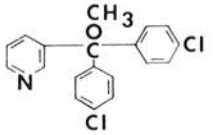
Effects of substitution in the R position of the alpha carbon.—Analogues in the methane and methanol series were usually equally fungicidal against the three turf diseases, but one exception was noted. All three diseases were controlled by 3[bis-(4-chlorophenyl)-methyl] pyridine; whereas, α,α-bis(4-chlorophenyl)-3-pyridinemethanol was inactive against leaf spot and brown patch (Table 3). Substitution of chloro, amino, or methoxyl groups in place of hydrogen or hydroxyl on the alpha carbon resulted in poor fungicidal activity against *Rhizoctonia* brown patch, but did not affect control of the other diseases.

Substitution on phenyl groups.—Attempts were made to increase efficacy of the pyridine alkanes and carbinols by substitutions on the phenyl groups. The basic structure for these modifications is α,α-diphenyl-3-pyridinemethanol (Table 4). This compound gave good control of all three diseases at 2.0 lb./acre. Substitution of a chlorine in the para position on one ring did not affect activity appreciably. Substitution in the para position of both phenyl groups reduced efficacy against dollar spot, and eliminated its efficacy against brown patch and leaf spot. A similar loss of fungicidal activity occurred when methoxyl or methyl groups were attached in both para positions. Substitution of dimethylamino groups resulted in a loss of activity against *Rhizoctonia* and *Sclerotinia,* but did not appreciably lessen efficacy against *Helminthosporium.*

Activity almost equal to that of the parent compound was obtained by substitution of chlorines in the 2 and 4 position or by placing both in the 2 position. A complete loss of activity occurred when an additional phenyl group was added to one of the phenyl rings to give α-(4-biphenyl)-α-phenyl-3-pyridinemethanol (Table 4).

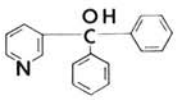
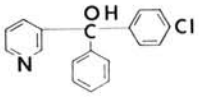
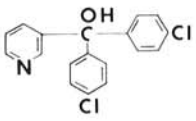
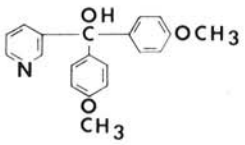
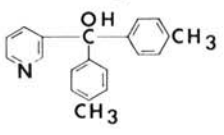
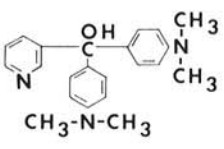
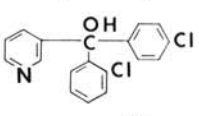
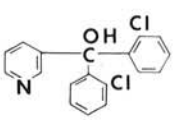
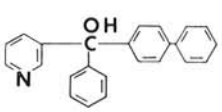
Cycloaliphatic substitution on the alpha carbon.—Fungitoxicity increased when certain cycloaliphatic groups were substituted for phenyl or chlorophenyl

TABLE 3. Fungicidal activity (at 2.0 lb./acre of active ingredient) of pyridine alkane and carbinol compounds with substitutions in the R position

Fungicide		Disease severity rating		
Structure	Name	*Helminthosporium* leaf spot	*Rhizoctonia* brown patch	*Sclerotinia* dollar spot
	3-[Bis(4-cholorophenyl) methyl] pyridine	3[a]	4	4
	α,α-Bis(4-chlorophenyl)-3-pyridinemethanol	1	1	3
	3-[Chloro-bis(4-chloro-phenyl) methyl] pyridine	4	2	4
	3-[Amino-bis(4-chloro-phenyl) methyl] pyridine dihydrochloride	4	3	4
	3-[Bis(4-chlorophenyl)-methoxymethyl] pyridine	3	2	4

[a] 5 = No disease; 4 = 1-10% leaf area diseased; 3 = 10-40%; 2 = 40-80%; 1 = 80-100%.

TABLE 4. Fungicidal activity (at 2.0 lb./acre of active ingredient) of pyridine carbinol compounds with substitution on phenyl groups attached to the R_1 and R_2 positions

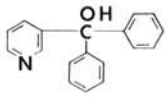
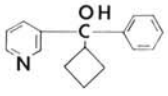
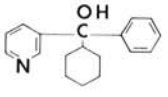
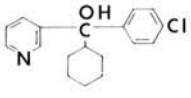
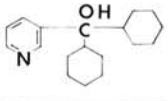
Fungicide		Disease severity rating		
Structure	Name	*Helminthosporium* leaf spot	*Rhizoctonia* brown patch	*Sclerotinia* dollar spot
	α,α-Diphenyl-3-pyridinemethanol	5[a]	4	5
	α-(4-Chlorophenyl)-α-phenyl-3-pyridinemethanol	4	5	5
	α,α-Bis(4-chlorophenyl)-3-pyridinemethanol	1	1	3
	α,α-Bis(4-methoxyphenyl)-3-pyridinemethanol	1	1	3
	α,α-Bis(*p*-tolyl)-3-pyridinemethanol	1	1	3
	α,α-Bis(4-dimethylaminophenyl)-3-pyridinemethanol	4	2	1
	α-(2-Chlorophenyl)-α-(4-chlorophenyl)-3-pyridinemethanol	4	5	5
	α,α-Bis(2-chlorophenyl)-3-pyridinemethanol	3	5	5
	α-(4-Biphenyl)-α-phenyl-3-pyridinemethanol	1	1	1

[a] 5 = No disease; 4 = 1-10% leaf area diseased; 3 = 10-40%; 2 = 40-80%; 1 = 80-100%.

moieties in R_1 and R_2 positions on the alpha carbon atom (Table 5). For example, α,α-diphenyl-3-pyridinemethanol at 0.5 lb./acre resulted in 2,2,5 ratings on leaf spot, brown patch, and dollar spot, respectively. The α-cyclobutyl-α-phenyl, α-cyclohexyl-α-phenyl, and α-4-chlorophenyl-α-cyclohexyl-3-pyridinemethanols gave virtually perfect disease control at 0.5 lb./acre. The bis-cyclohexyl analogue was not as effective against leaf spot at this rate, but was equally active against each of the other two. Further studies at rates as low as 0.015 lb./acre indicated that cyclohexyl-containing pyridine compounds were the most active in the series.

Determination of ED_{50} *and* ED_{95} *values.*—*Sclerotinia* dollar spot was used to determine ED_{50} and ED_{95} values of the three most active cyclohexyl-pyridine compounds. All tests were run with wettable powder formulations, and three reference compounds were included in each test for comparative purposes (Table 6). The cyclohexyl-phenyl and bis-cyclohexyl compounds were more effective at lower dosages and were less variable than the reference fungicides. Disease severity between tests differed, as demonstrated by the variation in ac-

TABLE 5. Fungicidal activity (at 0.5 lb./acre of active ingredient) of pyridine alkane and carbinol compounds when cycloaliphatic groups were substituted for phenyl or chlorophenyl groups in R_1 and R_2 positions

Fungicide		Disease severity rating		
Structure	Name	*Helminthosporium* leaf spot	*Rhizoctonia* brown patch	*Sclerotinia* dollar spot
	α,α-Diphenyl-3-pyridinemethanol	2[a]	2	5
	α-Cyclobutyl-α-phenyl-3-pyridinemethanol	5	5	5
	α-Cyclohexyl-α-phenyl-3-pyridinemethanol	4	5	5
	α-(4-Chlorophenyl)-α-cyclohexyl-3-pyridinemethanol	5	5	5
	α,α-Bis(cyclohexyl)-3-pyridinemethanol	3	5	5

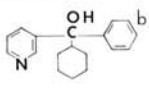
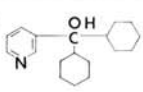
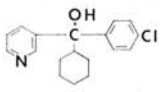
[a] 5 = No disease; 4 = 1-10% leaf area diseased; 3 = 10-40%; 2 = 40-80%; 1 = 80-100%.

tivity and high dosage rates of the reference compounds required to give 95% disease control. The degree of within-test and between-test variability associated with each compound may be assessed by comparing the sizes of the 0.95 confidence intervals present with each compound end point listed in the table.

Fungicidal activity of pyridine fungicides against Sclerotinia dollar spot in field studies.—Since many greenhouse fungicide test results differ from the data obtained under field conditions, the activity of selected pyridine analogues was tested in field plots. The compounds selected for field tests were α-cyclohexyl-α-phenyl-3-pyridinemethanol; α,α-bis(cyclohexyl)-3-pyridinemethanol; and α-(4-chlorophenyl)-α-cyclohexyl-3-pyridinemethanol. The bis-cyclohexyl and cyclohexylphenylpyridine compounds were effective at low rates of application throughout the summer (Fig. 1). A rate of 0.5 lb./acre every 7 days, 1.0 lb. every 14 days, or 2.0 lb. every 21 days controlled dollar spot. The chlorophenylcyclohexyl analogue was less active under field conditions, and gave acceptable control only at a rate of 1.0 lb./acre or greater applied weekly.

DISCUSSION.—Several compounds in the pyridine alkane and carbinol series were fungicidal, but this activity could be altered by chemical modification. Antifungal properties were generally poor if active groups were substituted in any but the 3 position of the pyridine ring. Groups occupying the R position on

TABLE 6. ED_{50} and ED_{95} levels and their 0.95 confidence intervals obtained from Astoria bentgrass turf plugs inoculated with *Sclerotinia homoeocarpa*[a]

		Daconil 2787	Dyrene	Tersanom	 [b]		
Test A	ED_{50}	>1.8[c]	0.28 ± 0.04	5.1 ± 2.8	0.07 ± 0.09	0.08 ± 0.03	1.0 ± 1.0
	ED_{95}	>1.8	1.2 ± 0.4	>10	0.3 ± 0.01	0.35 ± 0.05	>1.8
Test B	ED_{50}	2 ± 3	7.4 ± 3.3	3.6 ± 3.6	0.7 ± 0.23	0.07 ± 0.06	0.26 ± 2.4
	ED_{95}	>5.6	>18	16 ± 4	0.29 ± 0.27	0.29 ± 0.7	>0.18
Test C	ED_{50}	12 ± 5	>18	11 ± 1	0.04 ± 0.06	>0.02	0.3 ± 0.04
	ED_{95}	>18	>18	>18	0.17 ± 0.12	>0.02	>5.6

[a] End points and confidence intervals obtained by least squares regression analysis of log transformed per cent disease.
[b] The three compounds, left to right, are α-cyclohexyl-α-phenyl-3-pyridinemethanol; α,α-bis(cyclohexyl)-3-pyridinemethanol; and α-(4-chlorophenyl)-α-cyclohexyl-3-pyridinemethanol.
[c] Indicates highest level (lb./acre a.i.) tested did not reach the calculated end point.

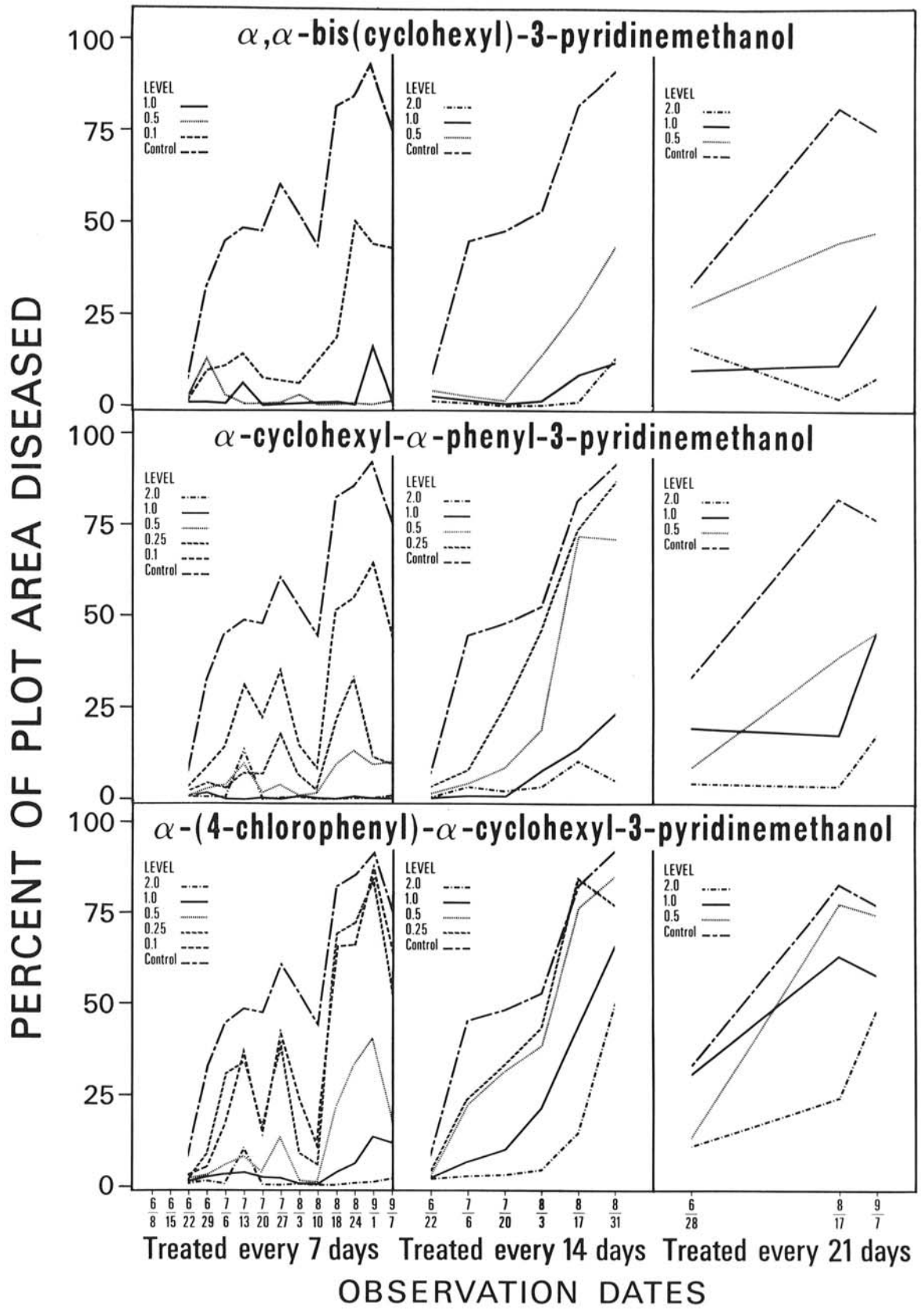


Fig. 1. Control of *Sclerotinia* dollar spot on Penncross bentgrass in the field with applications of three related cyclohexyl-pyridine compounds every 7, 14, and 21 days during the summer. Treatment level is expressed in lb./acre of active ingredient.

the alpha carbon were equally important for maximum activity. Replacement of the hydrogen of 3-[bis-(4-chlorophenyl)methyl] pyridine by a hydroxyl group destroyed most of the fungicidal properties. A similar replacement by chloro, amino, or methoxyl groups reduced activity against *Rhizoctonia* brown patch without significant change in the fungicidal properties against *Helminthosporium* leaf spot or *Sclerotinia* dollar spot. Apparently dollar-spot activity was affected less by substitution than either brown patch or leaf spot. Activity against the latter two diseases was rather easily lost.

When R_1 and R_2 were phenyl groups, activity varied widely with substitution on the aromatic rings. A chlorine in the 4 position of one ring did not alter fungicidal properties significantly over the unsubstituted diphenyl parent. An additional chlorine placed in the 4 position of the other ring, giving α,α-bis(4-chlorophenyl)-3-pyridinemethanol, resulted in the complete loss of activity against the turf pathogens. However, this compound was the most active against powdery mildew, as reported by Brown et al. (1). Activity was lost with methoxyl, methyl, or dimethylamino groups substituted in the 4 position of both phenyls. Activity comparable to the unhalogenated parent resulted if chlorine was attached to the 2 position of both rings or the 2,4 position on one ring.

Maximum fungicidal activity was obtained in the pyridine alkane and carbinol series when either R_1 or R_2 or both were cycloaliphatic groups. This type of structure possesses activity in the field against *Sclerotinia* at low rates of application. The only materials tested that were effective at rates lower than 0.5 lb./acre of active ingredient contained a cyclohexyl or cyclobutyl group in the molecule. The two most active compounds were found to be α-cyclohexyl-α-phenyl-3-pyridinemethanol and α,α-bis(cyclohexyl)-3-pyridinemethanol.

ED_{50} and ED_{95} comparisons between the most active cycloaliphatic compounds and the reference materials on *Sclerotinia* dollar spot demonstrated the activity of these fungicides at lower rates of application than the commercial reference compounds.

Results from field studies confirmed the fungicidal activity of the bis-cyclohexyl and phenyl-cyclohexyl pyridines, and indicated that 4-chlorophenyl-cyclohexyl compound was only slightly active. The reasons for this reduction in activity are not clear, but may be due to formulation problems rather than to a structural phenomenon. It is important that the dosage of the effective fungicides increases exponentially with increase of time between applications in the field. This would minimize the amount of labor normally required in weekly applications under severe epiphytotics of dollar spot.

Speculation on mode of action of these compounds is not possible at this time.

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