

listed in Table II. Without exception the  $\alpha$ -substituted acetamides thus formed were completely inactive as pre-emergence herbicides at the high rate of 25 pounds per acre.

If the activity of the  $\alpha$ -chloroacetamides were due solely to the chemical reactivity of the chlorine atom, the  $\alpha$ -chloropropionamides would be expected to possess activity, since the chemical reactivity of the chlorine atom in the two types of compounds should not differ greatly. Table III clearly illustrates that the  $\alpha$ -chloropropionamides are completely lacking in pre-emergence herbicidal activity at 25 pounds per acre. It may well be that enzymatic processes are operative which are incapable of utilizing the  $\alpha$ -chloropropionamides.

Table III also indicates that the position and number of chlorine atoms in the propionamides are not important in enhancing the activity of this class of

compounds. The diallyl and 3-methoxypropyl amides of  $\alpha,\alpha$ -chloropropionic acid (Dalapon) show no activity as pre-emergence herbicides in these tests. The chlorobutyramides are similarly devoid of activity, as illustrated by examples in Table III.

Biological activity involves not only structural considerations as illustrated above, but also biochemical and physicochemical considerations. The relative activities of the haloacetamides are undoubtedly the composite result of numerous properties of the chemicals and plants. Work is in progress in these laboratories to determine the importance and interrelationship of these various factors with respect to herbicidal activity (2).

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## PESTICIDAL ACTIVITY AND STRUCTURE

# Structural Effect of Some Organic Compounds on Soil Organisms and Citrus Seedlings Grown in an Old Citrus Soil

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A study was made of the effect of saturated and unsaturated alcohols, halides, acids, esters, amides, and some commercial fumigants on the soil organisms and growth of sweet orange seedlings in an old citrus soil. The organisms examined included the citrus nematode, *Tylenchulus semipenetrans* Cobb, fungi, and bacteria. It was concluded that high toxicity to these organisms, and citrus, is associated with halides and alcohols containing  $\alpha,\beta$ -unsaturation. Several halogen derivatives were more effective against the citrus nematode than some of the commercial fumigants now in use. Some chemicals were found to stimulate growth of *Trichoderma viride*, and indirect biological control of certain pathogenic soil organisms might be achieved by exploitation of this observation.

SOIL FUMIGATION for the control of nematodes, pathogenic fungi, bacteria, and other detrimental soil organisms is coming into increasing agricultural use (75). Fumigation of old citrus land before planting is becoming a common practice in California because of the substantial increases in

yields obtainable (3, 7). The fumigants commonly used for citrus soils are D-D (dichloropropene-dichloropropane mixture), EDB (1,2-dibromoethane), and carbon disulfide.

When a citrus grove becomes unproductive because of nematodes or other detrimental organisms, the trees must

be removed before the land is fumigated and replanted. These trees would not be lost if they could be treated in place with some nonphytotoxic fumigant. Alternate row fumigation with the trees in place is now being tried by some growers (8) and tested experimentally, but the practicability of this is yet unknown.

The chief purpose of this research has been to find some organic chemical relatively nontoxic to citrus, which will increase the growth of citrus in old citrus soil either by killing the detrimental organisms or by selectively encouraging microorganisms antagonistic to the pathogenic organisms present. Another objective has been to determine the relationship between chemical structure of various organic compounds and their toxicity to citrus, fungi, nematodes, and bacteria. A study of this type may provide soil fumigants much better than those now in use. This report summarizes the progress made thus far in relating chemical structure to biocidal activity.

### Materials

The chemical compounds tested thus far have been obtained from commercial sources or prepared according to methods described in the literature (Table I).

The old citrus soil chosen for the screening program was a Yolo loam that was obtained in 2-ton quantities from a 15-year-old lemon orchard of the Limoneira Co., Santa Paula, Calif. Samples consisted of a composite of soil from the 6- to 48-inch depth. The land had been cropped to citrus for 46 years, and the growth of orange seedlings in this soil in the greenhouse was poor when compared with that of citrus in the same soil prefumigated with D-D, propylene oxide, or other soil fumigants. The soil as brought from the field was screened through  $\frac{1}{4}$ -inch mesh, mixed well, and held in bulk storage in bins.

Analyses were made of this soil and are as follows: pH, 7.7; exchange capacity, 18.9 meq. per 100 grams; moisture holding capacity, 48%; field capacity, 25%; organic matter, 0.91%; sand, 56.2%; silt, 32.6%; clay, 11.2%.

### Methods

Samples of soil from the stock supply having a moisture content of 8 to 12% were brought to the laboratory and placed in 1-quart Mason jars in 600-gram portions (dry-weight basis). The compounds to be tested were added at 0, 2.5, 25, 250, and 1000 p.p.m., dissolved in either acetone or water as a solvent. Each concentration was replicated four times. Each treatment received the same volume of the solvent, whereas the check received solvent alone.

Two different methods of addition were used. Compounds with low boiling points will normally diffuse throughout the soil on standing and therefore were added directly to the jars containing the soil, using 0.2 ml. of acetone or 0.2 or 1 ml. of water. The tops to the jars were then replaced and the jars rotated 50 times end over end. Compounds

which were solids or liquids with high boiling points, in 1 ml. of acetone or water, were sprayed onto the soil to ensure uniform distribution. The soil was placed in a 2-liter evaporating dish on a phonograph-type turntable. Two curved aluminum blades mounted above the turntable acted as plows. An atomizer was used to spray the solution while the turntable was rotated at 55 r.p.m.

The mixtures were then transferred back to the Mason jars, which were rotated 50 times end over end to complete the mixing. To determine whether the mixing technique with solids and liquids of high boiling points was satisfactory, an acetone solution of anthracene was incorporated as described above, and the soil was examined under an ultraviolet light. Fluorescence was noticed throughout the whole soil mass.

Sweet orange seedlings, 2 inches in height, were then planted in three replicates of each of the four concentrations, and in three replicates of an untreated sample of soil, and immediately watered to prevent loss of volatile chemicals. All of these samples had been adjusted to 100 p.p.m. inorganic nitrogen. The remaining samples, consisting of one replicate of each of the four concentrations and an untreated sample, were incubated (with the tops to the quart jars in place) for 7 days at room temperature (20° to 25° C.) and then examined for the effect of the chemical on the citrus root nematode, fungi, and bacteria plus actinomycetes.

The citrus root nematode was determined by a modification of the Baermann funnel technique; fungi were determined by the dilution plate procedure, using peptone, dextrose, and rose bengal-streptomycin medium (20); and bacteria including actinomycetes (hereafter referred to as bacteria), were determined by using a mineral medium containing small amounts of peptone and dextrose. According to this procedure the soil contained approximately 2000 nematodes per 50 grams, 100,000 fungi per gram, and 10,000,000 bacteria per gram.

After growing in the quart jars for about 5 months, the plants were harvested and dried at 60° C. for 2 days. The weights of the tops and roots were then recorded to determine the effects of the various concentrations on growth.

### Results

The toxicities of some of the compounds tested thus far to nematodes, fungi, bacteria, and citrus are shown in Table I, where the concentration of chemical required to kill the plants and bring about 85 to 95% and 95 to 100% control of the soil organisms is indicated. None of the compounds increased the growth of sweet orange seedlings under the conditions of this

testing procedure. Interesting data were obtained, however, on the relationship between chemical structure and toxicity to nematodes, fungi, bacteria, and citrus.

**$\alpha,\beta$ -Unsaturation.** Examination of Table I shows that saturated alcohols, chlorides, bromides, iodides, acids, esters, and amides were less toxic to citrus seedlings, nematodes, fungi, and bacteria than derivatives containing  $\alpha,\beta$ -unsaturation. This is well illustrated by comparison of 1-pentanol (I) with allyl alcohol (III), propargyl alcohol (IV), and 2-buten-1-ol (V); 1-chloropentane (VIII) with allyl chloride (XIV) and propargyl chloride (XXI); 1-chloro-2-methylpropane (IX) with 3-chloro-2-methyl-1-propene (XVII); 1-iodopropane (XXVIII) with allyl iodide (XXIX); propionic acid (XXXIV) with acrylic acid (XXXV); and acetamide (XLVI) with acrylamide (XLVII). The compounds 4-pentene-1-ol (II) and 5-chloro-1-pentene (X), in which the double bond was separated from the functional group by methylene groups, showed approximately the same activity as the corresponding saturated derivatives 1-pentanol and 1-chloropentane. These results indicate that  $\alpha,\beta$ -unsaturation in a compound is associated with high toxicity toward soil organisms and citrus.

**Monosubstituted Ethylene and Acetylene Derivatives.** In the series RX, where R =  $H_2C=CH$  and X =  $CH_2OH$  (III),  $CH_2Cl$  (XIV),  $CH_2Br$  (XXVI),  $CH_2I$  (XXIX),  $COOH$  (XXXV),  $COOCH_3$  (XLIII), or  $CONH_2$  (XLVII), the order of toxicity was as follows:

Citrus.  $CH_2I, CH_2OH > CH_2Br > CH_2Cl, COOCH_3, CONH_2 > COOH$

Nematodes.  $CH_2I > CH_2Br, CH_2Cl, CH_2OH > COOH, COOCH_3, CONH_2$

Fungi.  $CH_2I > CH_2Br > CH_2Cl > CH_2OH > COOH, COOCH_3 > CONH_2$

Bacteria.  $CH_2I > CH_2Br, CH_2Cl > CH_2OH > COOH, COOCH_3, CONH_2$

In the series R'X, where R' =  $HC\equiv C$  and X =  $CH_2OH$  (IV),  $CH_2Cl$  (XXI),  $CH_2Br$  (XXVII),  $COOH$  (XL), or  $COOCH_3$  (XLIV), the order of toxicity was:

Citrus, Nematodes, and Fungi.  $CH_2Br > CH_2OH, CH_2Cl, COOCH_3 > COOH$

Bacteria.  $CH_2Br > CH_2OH > CH_2Cl > COOCH_3 > COOH$

Comparison of R with R', keeping X constant, shows that the acetylene derivatives were more phytotoxic than the ethylene derivatives except for allyl alcohol, which was more toxic than propargyl alcohol. In the series RX

**Table I. Toxicity of Various Organic Compounds to Nematodes, Fungi, Bacteria plus Actinomycetes, and Sweet Orange Seedlings in Old Citrus Soil**

	Compound	Source	Nematodes <sup>a</sup>	Fungi <sup>a</sup>	Bacteria plus Actinomycetes <sup>a</sup>	Sweet Orange Seedlings <sup>b</sup>	Method
Alcohols							
I.	1-Pentanol	Eastman Kodak Co.	2	2	2	+	
II.	4-Pentene-1-ol		2	0	0	+	(5)
III.	Allyl alcohol	Eastman Kodak Co.	6	3	2, 3	+++	
IV.	Propargyl alcohol	General Aniline and Film Corp.				++	
V.	2-Butyn-1-ol		6	4	4	+	(12)
VI.	2-Methyl-3-butyn-2-ol	Air Reduction Chem. Co.	0	0	0	-	
VII.	2-Butyn-1,4-diol	General Aniline and Film Corp.	4	0	2	++	
Chlorides							
VIII.	1-Chloropentane		4	1	2	+	(24)
IX.	1-Chloro-2-methylpropane	Eastman Kodak Co.	0	0	0	-	
X.	5-Chloro-1-pentene		4	2	2	+	(17)
XI.	1,2-Dichloroethane	Eastman Kodak Co.	4	3	2	+	
XII.	1,2-Dichloropropane	Eastman Kodak Co.	4	2	0	+	
XIII.	1,2,3-Trichloropropane	Eastman Kodak Co.	6	2	1	+++	
XIV.	Allyl chloride	Eastman Kodak Co.	6	4	4	+	
XV.	2,3-Dichloro-1-propene	Eastman Kodak Co.	7	3	2, 3	++	
XVI.	3,3-Dichloro-1-propene		4	4	2, 3	+	(18)
XVII.	3-Chloro-2-methyl-1-propene	Eastman Kodak Co.	6	4	2	++	
XVIII.	1,3-Dichloro-2-butene <sup>c</sup>	Eastman Kodak Co.	6	4	4	++	
XIX.	<i>cis</i> -1,3-Dichloropropene <sup>d</sup>		8	5	4, 5	++	
XX.	<i>trans</i> -1,3-Dichloropropene <sup>d</sup>		6	4	2	++	
XXI.	Propargyl chloride	General Aniline and Film Corp.				++	
XXII.	1,4-Dichloro-2-butyne	General Aniline and Film Corp.	8	4	4	+++	
Bromides							
XXIII.	1-Bromobutane	Eastman Kodak Co.	5	2	1	+	
XXIV.	EDB 1,2-Dibromoethane	Eastman Kodak Co.	8	3	2, 3	++	
XXV.	1,2,3-Tribromopropane	Eastman Kodak Co.	8	2, 3, 5	0	++	
XXVI.	Allyl bromide	Eastman Kodak Co.	6	4, 5	4	++	
XXVII.	Propargyl bromide	General Aniline and Film Corp.				+++	
Iodides							
XXVIII.	1-Iodopropane	Eastman Kodak Co.	6	2	2	++	
XXIX.	Allyl iodide	Eastman Kodak Co.	8	6	6	+++	
Chloroalcohols							
XXX.	3-Chlorobuten-2-ol-1		5	4	4	++	(12)
XXXI.	3-Chloro-1-propanol	Eastman Kodak Co.	4	3	2	++	
XXXII.	<i>cis</i> -3-Chloropropen-2-ol-1		6	4	4	++	(11)
XXXIII.	<i>trans</i> -3-Chloropropen-2-ol-1		6	4	4	++	(11)

and R'X the compounds most toxic to nematodes, fungi, and bacteria were allyl iodide and propargyl bromide.

In general, the alcohols, esters, and halogen derivatives of R and R' were more toxic to citrus and the soil organisms than the amides and acids. Ethylene and acetylene derivatives containing more than one functional group also followed this trend.

**Acids, Esters, and Amides.** Esters, because of their greater lipid solubility, are more toxic than the corresponding free acids (9, 19). The following comparisons show that this was the case with acetylenic esters but not with the saturated and olefinic esters: methyl propiolate (XLIV) with propiolic acid (XL), dimethyl acetylenedicarboxylate (XLV) with acetylenedicarboxylic acid (XLI), methyl propionate (XLII) with propionic acid, and methyl acrylate (XLIII) with acrylic acid. The higher toxicity of the unsaturated acids than of the saturated propionic acid is in agreement with the report that unsaturation increases fungicidal activity (25). *N*-Alkyl substitution of acrylamide de-

creased toxicity to nematodes and increased toxicity to citrus. This is illustrated by *N*-*tert*-butylacrylamide (XLVIII) and *N,N'*-methylenebisacrylamide (XLIX).

**Commercial Fumigants.** The fumigants tested as reference compounds were EDB (XXIV), experimental nematocide 1 (L), D-D (LI), OS-1897 (LII), Vapam (LIII), and Crag Fungicide 974 (LIV). All of these fumigants were lethal to nematodes at 25 p.p.m. The best nematocide was OS-1897, since it produced the greatest reduction in the number of nematodes at 2.5 p.p.m. Crag Fungicide 974 and Vapam were the best fungicides, while only the latter and D-D showed high bactericidal activity.

**Nematocides.** The most toxic compounds tested were *cis*-1, 3-dichloropropene (XIX), 1,2-dibromoethane (XXIV), 1,2-dibromo-3-chloropropane (LII), 1, 2, 3-tribromopropane (XXV), 1,4-dichloro-2-butyne (XXII), propargyl bromide (XXVII), and allyl iodide. Of these only the last four showed 100% kill at 2.5 p.p.m.

The following comparisons illustrate that iodide is more toxic than bromide and bromide more toxic than chloride: 1-iodopropane (XXVIII), 1-bromobutane (XXIII), and 1-chloropentane (VIII); allyl iodide, bromide (100% control at 25 p.p.m.), and chloride (96% control at 25 p.p.m.); propargyl bromide and chloride; 1,2-dibromo- and 1,2-dichloroethane (XI); 1,2,3-tribromo- and 1,2,3-trichloropropane (XIII).

A previous report on the efficacy of halogenated hydrocarbons suggested that physical factors such as solubility in water, ability to dissolve wax, and vapor pressure were most important (6). The results presented here, together with the fact that all known reactions of alkyl halides are faster with iodide than the bromide and faster with the bromide than the chloride, indicate that toxicity is closely associated with reactivity.

Although the bromide fumigants were better than those containing chloride, the latter would be preferable for citrus, as this species is sensitive to bromide (21).

**Table I. Toxicity of Various Organic Compounds to Nematodes, Fungi, Bacteria plus Actinomycetes, and Sweet Orange Seedlings in Old Citrus Soil (Continued)**

	Compound	Source	Nematodes <sup>a</sup>	Fungi <sup>a</sup>	Bacteria plus Actinomycetes <sup>a</sup>	Sweet Orange Seedlings <sup>b</sup>	Method
Acids							
XXXIV.	Propionic	Eastman Kodak Co.	2	0	0	+	
XXXV.	Acrylic	Carbide and Carbon Chemicals Corp.	4	2	0	-	
XXXVI.	Crotonic	Eastman Kodak Co.	2	0	0	-	
XXXVII.	Methacrylic	Monomer-Polymer	2	2	0	+	
XXXVIII.	Sorbic	Carbide and Carbon Chemicals Corp.	2	0	0	+	
XXXIX.	Furoic	Quaker Oats Co.	2	0	0	+	
XL.	Propiolic		4	0	0	+	(1)
XLI.	Acetylenedicarboxylic		2	0	0	-	(1)
Esters							
XLII.	Methyl propionate	Eastman Kodak Co.	2	0	0	-	
XLIII.	Methyl acrylate	Eastman Kodak Co.	4	2	0	+	
XLIV.	Methyl propiolate		6	4	2	++	(1)
XLV.	Dimethyl acetylenedicarboxylate		4	4	1	++	(16)
Amides							
NLVI.	Acetamide	Eastman Kodak Co.	0	0	0	-	
NLVII.	Acrylamide	American Cyanamid Co.	4	1	0	+	
NLVIII.	<i>N-tert</i> -Butylacrylamide	American Cyanamid Co.	2	0	0	++	
NLIX.	<i>N,N'</i> -Methylenebisacrylamide	American Cyanamid Co.	4	0	0	++	
Miscellaneous							
L.	Experimental nematocide 1. 40% mixture of 1,2 and 1,4-dichlorobutenes in 60% naphtha-type carrier	Carbide and Carbon Chemicals Corp.	6	2	0	++	
LI.	D-D. Mixture of 1,3-dichloropropene and 1,2-dichloropropane plus other chlorinated hydrocarbons	Shell Chemical Corp.	6	4	4	++	
LII.	OS-1897. 1,2-dibromo-3-chloropropane	Shell Chemical Corp.	8	2	2	++	
LIII.	Vapam. Na <i>N</i> -methylthiocarbamate	Stauffer Chemical Co.	6	6	4	+++	
LIV.	Crag fungicide 974. 3,5-dimethyltetrahydro-1,3,5-2H-thiadiazine-2-thione	Carbide and Carbon Chemicals Corp.	6	4, 6	2, 3	+++	

<sup>a</sup> 0 < 85% control at 1000 p.p.m. 1, 3, 5, and 7. 85-95% control at 1000, 250, 25, and 2.5 p.p.m., respectively. 2, 4, 6, and 8. 95-100% control at 1000, 250, 25, and 2.5 p.p.m., respectively.

<sup>b</sup> Nontoxic at 1000 p.p.m.

+, ++, +++ Lethal at 1000, 250, and 25 p.p.m., respectively.

<sup>c</sup> Purified by distillation, b.p. 68-70° C./100 mm.

<sup>d</sup> Prepared by fractional distillation of D-D.

**Table II. Effect of Organic Acids and Esters on Fungus Populations in an Old Citrus Soil**

Acid	Soil Treatment	Concentration, P.P.M.	Fungus Population
Propionic		250	<i>Trichoderma viride</i> plus <i>Fusarium solani</i> <sup>a</sup>
		1000	<i>T. viride</i> plus <i>F. solani</i> <sup>a</sup>
Acrylic <sup>b</sup>		250	<i>F. solani</i> plus a few <i>T. viride</i>
		1000	Fungicidal
Crotonic		250	<i>F. solani</i>
		1000	No major population
Methacrylic		250	No major population
		1000	Fungicidal
Sorbic		250	<i>F. solani</i> plus a few <i>T. viride</i>
		1000	<i>T. viride</i>
Furoic		250	<i>Penicillium</i> spp. plus a few <i>T. viride</i>
		1000	<i>P. spp.</i> plus <i>T. viride</i> <sup>a</sup>
Propiolic		250	No major population
		1000	No major population
Acetylenedicarboxylic		250	A few <i>T. viride</i>
		1000	<i>T. viride</i>
Ester			
	Methyl propionate	250	<i>F. solani</i>
1000		<i>F. solani</i>	
Methyl acrylate	250	<i>T. viride</i> , <i>F. solani</i> , <i>P. chrysogenum</i>	
	1000	Fungicidal	
Methyl propiolate	250	No major population	
	1000	Fungicidal	
Dimethyl acetylenedicarboxylate	250	Fungicidal	
	1000	Fungicidal	

<sup>a</sup> In approximately equal numbers.

<sup>b</sup> Examination of soil after citrus had been grown in soil showed following population: 250 p.p.m., predominantly *F. solani*; 1000 p.p.m., almost pure culture of *T. viride*.

**Fungicides.** The most active compounds were the  $\alpha,\beta$ -unsaturated halides, the commercial fumigants Vapam and Crag Fungicide 974, and the acetylenic esters and alcohols. Of these, the most toxic to fungi were allyl iodide and propargyl bromide, which were lethal at 25 p.p.m.

The allyl and propargyl halides show the same order of toxicity that was obtained with these compounds as nematocides—I>Br>Cl. Because methyl isothiocyanate is reported to be the toxic agent from the decomposition of Vapam, and this compound and  $\alpha,\beta$ -unsaturated halides are highly reactive towards nucleophilic reagents, perhaps their fungicidal activity is due to the disruption of some essential enzyme system by reaction with some required nucleophilic center.

**Activity of Some D-D Components.** Some of the components in this mixture (13) tested for their activity were allyl chloride, 2,3-dichloro-1-propene (XV), 3,3-dichloro-1-propene (XVI), *cis*- and

*trans*-1,3-dichloropropene (XIX, XX), and 1,2-dichloropropane (XII). All of these compounds were effective as nematocides and fungicides, some more so than others. It has been reported that the active nematocidal (22) and fungicidal (26) component in D-D is the 1,3-dichloropropene fraction, while the 1,2-dichloropropane fraction is inactive. The 1,3-dichloropropene fraction, consisting of the *cis* and *trans* isomers, was found to be more active than 1,2-dichloropropane, but the latter did show some nematocidal and fungicidal properties. No mention has been made that two other low-boiling components in this mixture, 2,3-dichloro-1-propene and 3,3-dichloro-1-propene, also have nematocidal and fungicidal activity. The 2,3-isomer was more toxic to nematodes; the 3,3-isomer was more toxic to fungi. The 2,3-isomer was more active as a nematocide than *trans*-1,3-dichloropropene but less active than the most toxic component *cis*-1,3-dichloropropene.

**Activity of *cis*-*trans* Isomers.** The *cis* and *trans* isomers of 1,3-dichloropropene and their hydrolysis products, *cis*- and *trans*-3-chloropropen-2-ol-1 (XXXII, XXXIII) were tested to determine what effect *cis*-*trans* isomerism would have on activity. The chloroalcohols were also tested, as some hydrolysis of allylic-type halides might be expected to take place in moist soil, so that part of the activity of this type of fumigant might be due to the alcohol.

Comparison of *cis*- with *trans*-1,3-dichloropropene shows that the *cis* isomer is more toxic to nematodes, fungi, and bacteria. Although not indicated, it was also slightly more toxic to citrus. One possible explanation is its greater reactivity. In nucleophilic displacement reactions the *cis* has been found to be more reactive than the *trans* isomer with the following compounds: 1,3-dichloropropene, 1,3-dichloro-2-methylpropene, and 1,2,3-trichloropropene (10).

A different relationship exists with the *cis*-*trans* isomers of 3-chloropropen-2-ol-1. The toxicity of the two isomers was the same but greater than that of the saturated derivative 3-chloro-1-propanol (XXXI).

Comparison of the *cis*-dichloride with the corresponding *cis*-chloroalcohol shows that hydrolysis of the allylic chloride lowers toxicity to the soil organisms. With the *trans* isomers, on the other hand, the dichloride was equal to the chloroalcohol in toxicity to nematodes and fungi, but less toxic to bacteria. Another example of the decrease in toxicity (to nematodes) due to hydrolysis is shown by comparing 1,3-dichloro-2-butene (XVIII) with 3-chlorobuten-2-ol-1 (XXX).

From the results with these compounds, and the fact that diethyl chlorofumarate was reported (9) to be more active

fungistatically than diethyl chloromaleate (*trans* more active than *cis*), it would appear that the activity of *cis*-*trans* substituted ethylene is a function not only of the arrangement about the double bond but also of the organism involved.

**Bactericides.** The most toxic compounds were the  $\alpha,\beta$ -unsaturated halides, Vapam, the unsaturated chloroalcohols, and the acetylenic alcohols, propargyl alcohol and 2-butyne-1-ol. Of these, the most active was allyl iodide. Of the two other acetylenic alcohols tested, 2-butyne-1,4-diol (VII) and 2-methyl-3-butyne-2-ol (VI), the former was only slightly active, while the latter was completely inactive, not only to bacteria but to nematodes, fungi, and citrus. This would suggest that an unhindered hydroxyl group  $\alpha,\beta$  to a triple bond is necessary for bacterial activity.

**Development of Specific Fungus Populations.** Certain acids and esters at high concentrations produced predominant fungus populations in this old citrus soil (Table II). Sorbic and acetylenedicarboxylic acid (XXXVIII, XLI) stimulated the development of an almost pure culture of *Trichoderma viride* at 1000 p.p.m., crotonic acid stimulated growth of *Fusarium solani*, acrylic and propionic acid stimulated *F. solani* plus *T. viride*, while furoic acid (XXXIX) stimulated a *Penicillium* species and *T. viride* in about equal numbers at 1000 p.p.m.

These results suggest possibilities in the solution of one of the major problems in agriculture—namely, indirect biological control of such pathogenic fungi as *Phytophthora*, *Pythium*, *Armillaria*, and *Rhizoctonia* spp. Since *T. viride* is known to be antagonistic to these organisms (2, 23), stimulation of *T. viride* in diseased soil by the addition of these compounds may be the answer to this problem. It remains to be seen whether the growth of *T. viride* is a function of the acid, soil type, initial fungus population, other factors, or a combination of these. Preliminary results with two other soils, one infested with *Phytophthora cinnamomi* (causal agent of avocado root rot) and the other an old walnut soil, indicate that other factors besides the structure of the acid are involved. This problem is under further investigation.

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