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# CHEMISTRY

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## Abstract

## Full Text

CHEMISTRY

B. G. BOLDYREV, K. A. GAR, and N. V. EVTEEVA

# ESTERS OF THIOSULFURIC ACIDS—NEW FUNGICIDAL AGENTS

(Presented by Academician S. I. Vol'fkovich, January 13, 1960)

The antimicrobial activity of esters (I) of thiosulfuric acids, known since the second half of the last century, has been studied only recently <sup>(1)</sup> in connection with the fact that, in their structure, they are close to esters (II) of thiosulfonic acids, among which is the natural antibiotic allicin



(I)

(II)

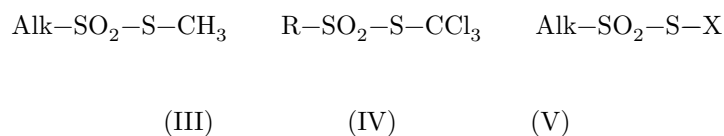
Like compounds (II), esters of thiosulfuric acids possess a broad spectrum of antimicrobial action and, in *in vitro* experiments, exhibit bacteriostatic and bactericidal action against gram-positive, gram-negative, and acid-resistant bacteria, various fungi, protozoa, etc.; the investigation was carried out by the Institute of Microbiology of the Academy of Sciences of the Ukrainian SSR on 35 species of microorganisms and in all cases gave positive results <sup>(1)</sup>.

Esters of thiosulfuric acids showed still higher activity when their action was studied on 40 different strains of 22 species of phytopathogenic bacteria <sup>(2)</sup>; at the same time they also display properties of stimulators of plant development, owing to which the use of esters (I) as agents for presowing treatment of seeds of grain, vegetable, and industrial crops gives a sharp reduction in the incidence of plant bacterioses, shifts the phases of their development toward early maturation, and, as a result, significantly increases their yield.

In carrying out field experiments, in a number of cases a fungicidal action of the same compounds was also observed—a reduction in the infection of barley, maize, etc., by smut.

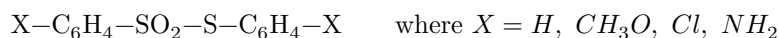
For this reason we considered it of interest to study broadly the fungicidal properties of esters of thiosulfuric acids and undertook the present investigation. As objects of study, we selected, first of all, alkyl esters of alkanethiosulfuric acids, which possess the highest antimicrobial activity, and, in particular, methyl esters (III).

It was also of interest to study the fungicidal properties of trichloromethyl esters (IV), which, according to American investigators (<sup>3</sup>), possess high fungicidal activity. The latter seemed to us all the more worthy of attention because we did not consider it possible to agree with the opinion of these authors on the equivalence of the fungicidal properties of trichloromethyl esters of various thiosulfuric acids, irrespective of the nature of the radical R (formula IV). On the basis of the results of our earlier studies (<sup>1</sup>), it followed that trichloromethyl esters of alkanethiosulfuric acids should be expected to possess higher activity than analogous esters of arenethiosulfuric acids.



for R = Alk, Ar                      for Alk = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>

for X = H, CH<sub>3</sub>O



(VI)

This choice of objects of study made it possible at the same time to reveal the influence of the trichloromethyl grouping itself—the replacement of the hydrogens of the methyl group by chlorine atoms—on the fungicidal properties of thiosulfonic acid esters.

The objects of study also included certain aryl esters (V) and (VI) of alkane- and arenethiosulfonic acids, which made it possible to determine more fully the relationship between structure and fungicidal activity in this class of compounds.

The study of the fungicidal activity of thiosulfonic acid esters was carried out by the toxicological laboratory of the Scientific Institute for Fertilizers and Insec-

#### Table 1

**Fungicidal activity of thiosulfonic acid esters  $R\text{-SO}_2\text{-S-R}'$**

No.	R	R'	Concentration of preparation by active ingredient, %					
			Diplodia zeae	Alternaria radicina	Verticillium dahliae	Fusarium vasin-tum	Fusarium oxysporum	
1	iso-C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	0.02	100	79	100	100	82
1	iso-C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	0.01	100	70	100	48	53
2	C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	0.02	100	90	100	100	100
2	C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	0.01	100	80	100	100	100
3	iso-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	0.02	100	90	100	100	100
3	iso-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	0.01	100	60	100	100	100
4	iso-C <sub>3</sub> H <sub>7</sub>	CCl <sub>3</sub>	0.02	100	100	100	100	100
4	iso-C <sub>3</sub> H <sub>7</sub>	CCl <sub>3</sub>	0.01	100	92	100	100	100
5	C <sub>4</sub> H <sub>9</sub>	CCl <sub>3</sub>	0.02	100	100	100	100	100
5	C <sub>4</sub> H <sub>9</sub>	CCl <sub>3</sub>	0.01	100	92	100	100	100
6	iso-C <sub>4</sub> H <sub>9</sub>	CCl <sub>3</sub>	0.02	100	100	100	100	100
6	iso-C <sub>4</sub> H <sub>9</sub>	CCl <sub>3</sub>	0.01	100	79	100	100	100
7	<i>n</i> -ClC <sub>6</sub> H <sub>4</sub>	CCl <sub>3</sub>	0.05	53.8	100	100	61.6	100
7	<i>n</i> -ClC <sub>6</sub> H <sub>4</sub>	CCl <sub>3</sub>	0.01	0.0	74.4	72.0	48.1	22.8
8	<i>n</i> -CH <sub>3</sub> CONHC <sub>6</sub> H <sub>4</sub>	CCl <sub>3</sub>	0.05	18.8	71.8	100	100	35.9
8	<i>n</i> -CH <sub>3</sub> CONHC <sub>6</sub> H <sub>4</sub>	CCl <sub>3</sub>	0.01	16.3	64.2	16.0	77.0	5.7
9	<i>n</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	CCl <sub>3</sub>	0.025	0.0	68.6	60.0	32.7	23.3
9	<i>n</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	CCl <sub>3</sub>	0.01	0.0	51.5	26.7	9.7	7.2
10	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	0.04	100	100	100	100	84
10	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	0.02	90.3	80.0	76.2	60.0	56.7
11	CH <sub>3</sub>	<i>n</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	0.04	94.0	80.0	100	85.0	26.7

No.	R	R'	Concentration of preparation by active ingredient, %					
			Diplodia zeae	Alternaria radicina	Verticillium dahliae	Fusarium vasin-tum	Fusarium oxysporum	
11	CH <sub>3</sub>	<i>n</i> - CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	0.02	70.0	74.3	67.0	60.0	55.0
12	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	0.04	100	98	100	97	84
12	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	0.02	92.7	80.0	76.2	71.0	54.0
13	Same	<i>n</i> - CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	0.04	96.6	82.0	100	100	79.0
13	Same	<i>n</i> - CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	0.02	92.0	76.0	57.0	80.0	63.0
14	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	0.05	95.0	61.6	100	55.0	60.0
14	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	0.01	40.0	56.5	72.0	32.7	49.1
15	<i>n</i> -	<i>n</i> - ClC <sub>6</sub> H <sub>4</sub> ClC <sub>6</sub> H <sub>4</sub>	0.025	47.3	74.4	33.4	42.4	43.0
15	<i>n</i> -	<i>n</i> - ClC <sub>6</sub> H <sub>4</sub> ClC <sub>6</sub> H <sub>4</sub>	0.01	43.7	68.6	33.4	34.7	32.2
16	<i>n</i> -	<i>n</i> - CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	0.04	87.4	67.0	63.0	60.0	52.0
16	<i>n</i> -	<i>n</i> - CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	0.02	82.8	64.0	44.0	52.1	43.0
17	<i>n</i> -	<i>n</i> - NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	0.025	93.1	85.8	73.4	71.2	64.3
17	<i>n</i> -	<i>n</i> - NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	0.01	90.3	74.4	60.0	42.4	43.0
18	Figon (standard)		0.025	93.6	97.2	100	100	50.0
18	Figon (standard)		0.01	88.1	85.8	100	92.4	39.3
19	Captan (standard)		0.03	85.1	76.0	77.0	79.4	79.4
19	Captan (standard)		0.02	83.6	72.0	65.0	65.6	53.5

No.	R	R'	Concentration of prepa- ration by active ingre- dient, %	Fusarium				
				Diplodia zeae	Alternaria radic- ina	Verticillium dahliae	vasin- fec- tum	Fusarium oxys- porum
20	Zineb (stan- dard)		0.04	73.2	68.0	100	22.5	22.5
20	Zineb (stan- dard)		0.02	15.0	24.0	15.0	5.2	6.9

at the Ya. V. Samoilov Research Institute of Insectofungicides on five species of fungi—*Diplodia zeae*, *Alternaria radicina*, *Verticillium dahliae*, *Fusarium vasinfectum*, and *Fusarium oxysporum*—in laboratory experiments, by introducing the preparations in the form of acetone solutions of a definite concentration into an agar nutrient medium, onto which the test organisms were then inoculated; the results of the action of the esters were determined after five days of fungal growth. For comparison, analogous experiments were carried out with figon, captan, and zineb at the same concentrations of active ingredient.

The results of the study, given in Table 1, fully confirmed our assumptions. They showed that the trichloromethyl esters of alkanethiosulfonic acids are the most active fungicides of all the compounds (I) studied by us and exert, in *in vitro* tests, a considerably stronger effect on fungi than the analogous esters of arenethiosulfonic acids.

However, the trichloromethyl group is not responsible for the fungicidal properties of these compounds: replacement of the chlorine atoms by hydrogen atoms and thus conversion to the methyl esters of alkanethiosulfonic acids has little effect on the activity of these compounds; like the trichloromethyl esters of alkanethiosulfonic acids, they exert a considerably stronger effect on fungi than the trichloromethyl esters of arenethiosulfonic acids.

A particular influence of the nature of the acid radical *R* is also observed upon further transition to the aryl esters of thiosulfonic acids (V) and (VI). Whereas the aryl esters of methane- and ethanethiosulfonic acids (Nos. 10-13, Table 1) still exhibit high fungicidal activity and even surpass in their action the trichloromethyl esters of arenethiosulfonic acids (Nos. 7-9, Table 1), the aryl esters (VI) possess noticeably lower activity in comparison with the other esters (I). However, even in this case some of them (No. 17, Table 1) are not inferior

in their action to such active fungicides as captan, at the same concentration of active ingredient.

The results obtained allow one to recognize that esters of thiosulfonic acids and, especially, esters of alkanethiosulfonic acids are highly active fungicides and deserve more detailed investigation. Further field experiments should show the possibility and prospects of using them in agricultural practice.

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## CITED LITERATURE

1. B. G. Boldyrev, V. G. Drobot' ko et al., DAN, **121**, 924 (1958).
2. K. I. Bel' tyukova, B. G. Boldyrev, DAN, **117**, 500 (1957).

*Note: Figure translations are in progress. See original paper for figures.*

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