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Structure Acaricidal Activity Relationship of Some Sulfonate and Thiosulfonate Derivatives Against the Two-Spotted Spider Mite *Tetranychus urticae* (Koch.)

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Abstract: A series of sulfonate and thiosulfonate derivatives have been synthesized to examine their acaricidal activity against the two-spotted spider mite *Tetranychus urticae* (Koch.). Generally, most of the synthesized compounds showed good acaricidal activity against adults and larvae. thiosulfonate derivatives were more active than sulfonate derivatives against eggs. In addition, the most active compounds were synergized by mixing with piperonyl butoxide at 1:2 ratio, respectively and the result showed that piperonyl butoxide highly improved the acaricidal activity against adult females of *T. urticae*. Importantly, both sulfonate and thiosulfonate derivatives were highly synergized by piperonyl butoxide to be more effective than the standard acaricide.

Key words: Acaricidal activity, *Tetranychus urticae*, sulfonate, thiosulfonate, structure-activity relationship. Two-spotted spider mite

INTRODUCTION

Tetranychus urticae (Koch.), is considered to be one of the major pests attacking different agricultural crops such as cotton, vegetables, fruit and ornamental plants. The infestation is usually causing a great damage to the infested plants followed by a secondary infestation by various pathogens such as virus, bacteria and fungi. Recently, it has been reported to cause occupational allergic disease in greenhouse workers[7,15].

Therefore, numerous synthetic organic compounds differing markedly in their chemical configurations were investigated and proved to possess high acaricidal activity including, organophosphates (TEPP, naled, mevinphos, parathion, carbophenthion, chlorpyrifos and azinphosmethyl), carbamates (carbofuran, fenothiocarb and aldicarb), nitrophenol derivatives (dinocap, binapacryl, dinobuton and dinitrocyclohexylphenol)[10]. In a search for such type of compounds, the patent literature contains an enormous number of compounds that are reported to have beneficial agricultural effects. However, only a relatively small number that have the high level of acaricidal activity combined with the safe toxicological and environmental properties that are required for the use in agriculture.

One of the most important class of acaricide is the sulfur derivatives ,*i.e*, sulfide, sulfone, sulfite and sulfonate derivatives which have been reported to possess strong acaricidal activity with the absence of phytocidal-effects and toxicity for warm-blooded animals. The current research reports the successful preparation of a series of sulfonate and thiosulfonate derivatives to examine their acaricidal activity against the two-spotted spider mite *T. urticae*.

MATERIALS AND METHODS

General: Melting points were determined on a Kofler hot stage apparatus and were uncorrected. IR spectra were recorded on Unciam SP spectrometer. ^{1}H NMR spectra were recorded with a Varian 200 MHz. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) as internal standard and described as s (singlet), d (doublet), t (triplet), m (multiplet), or bs (broad singlet). $CDCl_3$ (deuterated chloroform) or DMSO (dimethylsulfoxide) were used as solvent. *J* (spin spin coupling constant) values are given in Hz. Column chromatography was performed on 230-400 mesh gel silica. All solvents were distilled and dried before use.

Synthesis of sulfonate derivatives (1a-g): To a solution of 1-naphthole (0.01 mol, 1.44 g) in dichloromethane (20 ml) at 0 ºC was added triethylamine (0.01 mol, 1.4 ml) followed by addition of (0.01 mol) of benzenesulfonyl chloride (1a) or *p*-methylphenylsulfonyl chloride (1b) or *p*-chlorobenzenesulfonyl chloride (1c). In preparation of compounds (1d-g), (0.01 mol, 1.45 g) of 8-hydroxyquinoline was added to (0.01 mol) of

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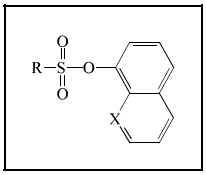
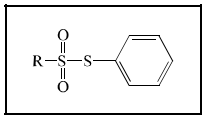
benzenesulfonyl chloride (1d) or *p*-toluenesulfonyl chloride (1e) or *p*-chlorobenzenesulfonyl chloride (1f) or methylsulfonyl chloride (1g). The flask was fitted with a condenser and stirred overnight at room temperature. After the reaction was completed, the mixture was poured into a separatory funnel and washed with distilled water (100 ml). The organic layer was dried by anhydrous sodium sulfate (15 -20 g) and the solvent was removed with a rotary evaporator. The residue was purified by silica gel column chromatography and eluted by ethyl acetate, hexane 2:3 to afford the desired compunds as solid crystals. The physiochemical properties and the corresponding spectroscopic data are shown in Table 1 and 2.

Synthesis of thiosulfonate derivatives (2a-d): Thiophenol (0.01 mol, 1.1 g) was dissolved in dichloromethane (20 ml), then triethylamine (0.01 mol, 1.4 ml) and (0.01 mol) of benzenesulfonylchloride (2a) or *p*-toluenesulfonylchloride (2b) or *p*-chlorobenzenesulfonylchloride (2c) or methylsulfonylchloride (2d) was added. The reaction was proceeded as above till the desired compounds (2a-d) were obtained. Organic layer was dried by anhydrous sodium sulfate (15 -20 g) and the solvent was removed with a rotary evaporator. The residues were purified by column chromatography on silica gel and eluted by a ethyl acetate: hexane 2:3 ratio to give solid crystals. The physiochemical properties and corresponding spectroscopic data are shown in Table 1 and 2.

Table 1: Physiochemical properities of sulfonate and thiosulfonate derivatives.



1a-g



2a-d

Compound	R	X	Yield (%)	m.p (°C)
1a	C_6H_5	C	70	108-110
1b	*p*-$CH_3C_6H_4$	C	77	77-78
1c	*p*-ClC_6H_4	C	75	81-83
1d	C_6H_5	N	56	114-115
1	*p*-$CH_3C_6H_4$	N	60	109-110
1f	*p*-ClC_6H_4	N	77	115-116
1g	CH_3	N	55	81-82
2a	C_6H_5	-	71	57-59
2b	*p*-$CH_3C_6H_4$	-	87	55-56
2c	*p*-ClC_6H_4	-	74	59-60
2d	CH_3	-	53	59-60

Acaricidal assay

Test animal: The infested cotton leaves were collected from the Agriculture Research Station of Alexandria University and transferred into the laboratory. The adults females were selected by a fine hair brush to castor leaves and maintained in a glass rearing chamber (80 x200 x80 cm) covered with a wire net. Mites were always transferred from old leaves to new ones. The colony was kept under laboratory conditions (25 ± 5°C, 60-70% relative humidity and 12 hr daily illumination[1].

Test chemicals: The test chemicals were initially dissolved in dimethylsulfoxide (DMSO) then diluted further with distilled water to achieve the desired final concentration of solvent (0.5%). A series of concentrations ranged from 10 to 1000 ppm were used. The standard acaricide propagite was used for comparison.

Bioassay techniques

Slide-dip technique (Adulticidal Screening): The method of Dittrich[3] was used as follows: A piece of double faced scotch tape was pressed tightly to the slide and 30 adult female mites were fixed to the tape on the dorsal part. The prepared slides were dipped in the toxicant solution and gently agitated for 5 seconds to ensure complete wetting then removed and placed on the edge of absorbent material for 15 minutes. The treated slides were put into holding chamber at 27°C and about 95% relative humidity and kept horizontally. Mites were examined for mortality after 24 hours of treatment under a microscope (10x to 20x). Mites which failed to respond when prodded lightly with a fine brush were considered to be dead.

Leaf disc-dip method (Ovicidal and Larvicidal Screening): Discs of about 2 cm in diameter of castor leaves were used[16]. Young and fully expanded leaves were selected and as soon as the discs can be faced up or down according to the preference of the mite species used. Discs were glued individually to glass petri-dish and five adult females were put on each disc then left for 24 hr to lay eggs. Females were removed and the eggs then were counted and the discs were immersed in the test liquid for 5 seconds with gentle agitation. The tested units were kept together with untreated controls in a holding chamber of about 25°C and 95% relative humidity. Assessment of the results was made when the hatched mites in the controls have reached the deutonymphal stage.

Synergistic effect: Piperonyl butoxide was used as synergist for the most active synthesized compounds against adult and egg stages of a *T. urticae*. Synergistic ratio (S.R) was calculated from using Hewlett formula[6].

Statistical analysis: LC_{50} (ppm) values with their fiducial limits for all treatment were determined by the probit-analysis method of Finney[5].

Table 2: Spectroscopic data of of sulfonate and thiosulfonate derivatives.

Entry	^{1}H-NMR (δ ppm)	IR (KBr) ν max cm^{-1}
1a	($CDCl_3$) 7.47 (8H, m), 7.91 (4H, m)	1371, 1186, 776, 762
1b	(*d*DMSO) 2.37 (3H, s, CH_3), 7.23 (1H, d, *J*7.6 Hz), 7.50 (5H, m), 7.90 (5H, m)	1368, 1179, 806, 771
1c	(*d*DMSO) 7.27 (1H, d, *J* = 7.6 Hz), 7.55 (3H, m), 7.72 (2H, d, *J* = 8.6 Hz), 7.95 (5H, m)	1374, 1188, 776
1d	(*d*DMSO) 7.62 (7H, m), 7.94 (2H, d, *J* = 8.6 Hz), 8.43 (1H, d, *J* = 8.4 Hz), 8.82 (1H, d, *J* = 4.2 Hz)	1372,1187, 784, 762
1e	(*d*DMSO) 2.37 (3H, s, CH_3), 7.41 (2H, d, *J*= 8.4 Hz, Ph), 7.57 (3H, m, quinolinoyl), 7.83 (2H, d, *J* = 8.2 Hz, Ph), 7.97 (1H, d, *J* = 8.2 Hz, quinolinoyl), 8.41 (1H, d, *J*= 8.4 Hz, quinolinoyl), 8.86 (1H, d, *J* = 4.2Hz, quinolinoyl)	3064, 1373, 1179, 776, 682
1f	($CDCl_3$) 7.34-7.38 (3H, m), 7.46 (1H, d, *J* = 7.8 Hz, quinolinoyl), 7.60 (1H, d, *J* = 7.6 Hz, quinolinoyl), 7.69 (1H, d, *J* = 8Hz, quinolinoyl), 7.88 (2H, d, *J* = 8.6 Hz, Ph), 8.07 (1H, d, *J* = 8.4 Hz, quinolinoyl), 8.73 (1H, d, *J* = 4.2 Hz, quinolinoyl)	3068, 1378, 1188, 782, 617
1g	(*d*DMSO) 3.62 (3H, s, CH_3), 7.80 (3H, m), 8.12 (1H, d, *J* = 7.2 Hz), 8.69 (1H, d, *J*= 8.6 Hz), 9.11 (1H, d, *J* = 4.8 Hz)	2979, 1356, 1175
2a	(*d*DMSO) 7.39 (6H, m, Ph), 7.54 (4H, d, *J* = 8.8 Hz)	1575, 1474, 1435, 1071
2b	(*d*DMSO) 3.39 (3H, s, CH_3), 7.39 (5H, m, Ph), 7.54 (4H, d, *J* = 7.0 Hz, Ph)	1575, 1474, 1434, 1070
2c	(*d*DMSO) 7.37 (5H, m, Ph), 7.53 (4H, d, *J* = 8.2 Hz, Ph)	1575, 1474, 1435, 1071
2d	(*d*DMSO) 3.48 (3H, s, CH_3), 7.38 (3H, t, *J* = 8.2 Hz, Ph), 7.53 (2H, d, *J* = 7.2 Hz, Ph)	1576, 1475, 1437, 1072

RESULTS AND DISCUSSION

Acaricidal activity of sulfonate derivatives: The acaricidal activity of sulfonate derivatives against adult females of *T. urticae* are shown in Table 3. These compounds are subdivided into two types, 1-naphthylsulfonate derivatives (1a-c) and quinolinoylsulfonate derivatives (1d-g). Generally quinolinoylsulfonate derivatives showed higher acaricidal activity against adult females of *T. urticae* than naphthylsulfonate derivatives. Naphthylsulfonate compounds such as compound 1b which have methyl group on *p*-position of the phenyl ring showed a high toxic effect with LC_{50} = 27 ppm against adult females of *T. urticae*. Replacing the methyl group in compound 1b with chlorine as in compound 1c reduced the acaricidal activity (LC_{50} = 110 ppm) (compound 1b versus 1c). The unsubstituted compound (1a) exhibited low acaricidal activity with LC_{50} = 278 ppm (compound 1a versus 1b or 1c). In comparison with standard acaricide (propargite), compound 1b showed a higher toxicity, approximately 2.5 fold while compound 1a was the lowest one in this regard.

In quinolinoylsulfonate derivatives (1d-g) the descending order of the toxicity against adult females of *T. urticae* (Koch.) was compound 1f > compound 1e>compound 1d > compound 1g with LC_{50} values 39, 85, 136, and >1000 ppm, respectively. Using of 8-hydroxyquinoline instead of 1-naphthol increased the acaricidal activity (1a versus 1d). Substitution of chlorine at p-position of the phenyl ring (1f) showed higher toxic effect than the standard acaricide, propargite, (approximately 1.8) fold. Replacing chlorine with methyl group reduced the acaricidal activity compared to chlorine. Also, the unsubstituted compound (1a) was less active one. In addition, replacing of phenyl ring as in the case of compound 1g by methyl group caused reduction in the activity against adult females of *T. urticae* (1g versus 1d-f).

Table 3: Acaricidal activity of sulfonate and thiosulfonate derivatives against adult females of *T. urticae* after 24 h.

Compound	LC_{50} (ppm) [a]	95% fiducial limits
1a	278	(372-207)
1b	27	(53-14)
1c	110	(145-83)
1d	136	(176-105)
1	85	(123-58)
1f	39	(64-23)
1g	>1000	-
2a	85	(119-60)
2b	13	(16-10)
2c	23	(33-16)
2d	38	(49-30)
Propargite	68	(78-59)

[a] Average based on three replicates (n=3), 20 animals each.

The obtained results are in agreement with Yoshinaga *et al*.[17,18] where, the aqueous suspension of *p*-methylthiophenylvinylsulfonate, Na-dodecylsulfonate, Na-dinaphthylmethanesulfonate and diatomaceous earth caused 100% mortality at 500 ppm to *T. urticae* (Koch.) on kidney-bean plant within 2 days. Kitagaki and Hideo[8] reported that 2-chloroethylchloromethane sulfonate, 2,2,2-trichloroethylchloromethane sulfonate, 1,3-dichloropropylchloromethane sulfonate, 3,3-dichloroallylchloromethanesulfonate and 5,5-dichloro-4-penten-1-ylchloro methanesulfonate killed a peresent ranged from 92 to 100 % of the adult females of carmine mites at 1000 ppm. In the present study, all sulfonate derivatives showed good acaricidal effect against the adult females of *T. urticae* except compound 1g.

Acaricidal activity of thiosulfonate derivatives: Four thiosulfonate compounds were prepared in this study

(Table 1) and their acaricidal activity were evaluated against adult females of *T. urticae* (Table 3). Replacing the oxygen with sulfur atom (sulfonate versus thiosulphonate) led to a dramatic increase in the acaricidal activity. This may be due to penetration increment and/or forming sulfide bridge in the mechanism of toxic action. Importantly, compound 2b was found to be the most toxic one and gave 5.15 fold more than the standard acaricide where methyl group was in *p*-position of the phenyl ring. In general, these derivatives except compound 2d were more toxic compared to sulfonate derivatives which may be attributed to the effect of sulfur atom. Kitagaki *et al.*[9] found that chloromethanesulfonate derivatives such as 5-(4-bromo-3-methylphenyl) chloromethane thiosulfonate were effective either in contact or in systemic action against several species of mites. This group of compounds showed promising activity and could be developed as acaricide agents.

Ovicidal and larvicidal activity of sulfonate derivatives: The results of sulfonate (1-naphthoyl or 8-quinolinoyl) derivatives are presented in Table 4. Most of the tested derivatives were moderatly active against eggs at 100 ppm. However, increasing the concentration up to 500 ppm led to an increase in the ovicidal activity. In addition, substitution with chlorine in *p*-position as in compound 1c increased the ovicidal activity up to 65 % mortality. At 1000 ppm, most of the derivatives showed high ovicidal activity particularly compound 1a (80% mortality).

The effect of this group on larvae was better where the kill %, reached up to 72 % (compound 1a) and the standared acaricide was 86% at the same concentration (100 ppm). Increasing the concentration up to 500 ppm gave high acaricidal activity (86 % in case of compound 1a). At concentration, 1000 ppm compound 1c, where the chlorine is at the *p*-position gave 100% mortality followed by compound 1b (88 % mortality) which containes a methyl group instead of the chlorine atom) and then compound 1a which gave 86 % mortality.(unsubstituted phenyl ring). The obtained results showed that chlorine atom at *p*-position play an important role in increasing thr acaricidal activity against eggs and larvae (Table 4).

Importantly, as a total kill %, the results indicated good acaricidal activity for those three prepared derivatives (1a-c) against both eggs and larvae particularly compound 1c which has chlorine atom at the *p*-postion of the phenyl ring. The reason of that phenomena could be due to either an increase in the stability of these compounds or to the high penetration through egg shell. The larval kill which has been recorded after hatching (after 6 days) were healthy but they killed after contact with the residual film of these derivatives.

The quinoline derivatives (1d-g) showed a lower effect against the eggs of *T. urticae* than the previous group except compound 1d which gave moderate ovicidal activity. However, in the case of larvicidal effect, all tested compounds were effective except 1g where phenyl ring was replaced with methyl group indicating the important role of the presence of the aromatic ring moiety in the molecule. At concentration of 100 ppm, compound 1e showed the higher effect (73 % mortality) against the larvae. The results as total kill % showed that the same trend of acaricidal activity especially the cholrine atom which improved the activity as in 1c and 1f (both *p*-chlorine substituted) gave 100 % tolal kill. Substitution with methyl group (compound 1e) or un-substituted phenyl ring (1d) exhibited good larvicidal activity. Replacing of the phenyl ring with methyl group (1d versus 1g) sharply decreased the larvicidal activity against *T. urticae*. Our present results coincides with an early study published by Brown[2]. He reported that benzenesulphonates are week insecticides but they are strong acaricides, suggesting a certain type of selectivity. Also, EL-Nawawy *et al.*[4] found that the most toxic compound was S-n-propyl-isothiouronium benzenesulphonate to *Tenebrio molitor*.

Table 4: Ovicidal and larvicidal activity of sulfonate and thiosulfonate derivatives against *T. urticae*.

Compound	Conc. (ppm)	Egg kill (%)	Larval kill (%)	Total kill (%)
1a	100	21	73	72
	500	31	86	88
	1000	80	86	96
1b	100	15	35	44
	500	32	72	76
	1000	62	88	95
1c	100	32	63	69
	500	65	78	90
	1000	71	100	100
1d	100	32	42	51
	500	57	76	87
	1000	74	87	96
1e	100	32	73	82
	500	36	83	89
	1000	40	88	93
1f	100	14	70	74
	500	27	81	87
	1000	53	100	100
1g	100	9	29	35
	500	17	40	50
	1000	40	57	74
2a	100	30	70	79
	500	94	85	99
	100	100	-	100
2b	100	25	59	69
	500	61	58	84
	1000	93	67	99
2c	100	29	49	64
	500	58	60	83
	1000	83	64	94
2d	100	24	44	58
	500	76	55	89
	1000	89	90	99
Propargite	100	50	87	98
	500	100	-	100
	1000	100	-	100

Ovicidal and larvicidal activity of thiosulfonate derivatives: Thiosulfonate derivatives 2a-d showed strong ovicidal and larvicidal activity compared to sulfonate derivatives 1a-g and to the standard, Proarigte (Table 4). The effects was moderate at 100 ppm. However, increasing the concentration up to 500 ppm highly increased the acaricidal activity and compet the standard as in compound 2a (94 % mortality,). The rest of these derivatives were more effective than sulfonate. Also, the larvicidal activity of thiosulfonate derivatives were good particularly compound 2a at 500 ppm (85% mortality). As a total kill %, compound 2a (unsubstituted phenyl ring) was considered to be the most promising one which could be developed as acaricide. However, substitution with methyl group or cholrine atom at *p*-position of the phenyl ring (2b or 2c) lead to a decrease in acaricial activity against eggs and larvae.

Synergistic effect of piperonyl butoxide to the most potent sulfonate and thiosulfonate derivatives against adult females of *T. urticae*: Synergists are usually of practical and economical importance in efficient control of insect. The use of piperonyl butoxide, sulfoxide or sesamex with the expensive pyrethroide, or carbaryl to increase the spectrum of activity or break the resistance of resistant strains of insects. Perhaps, they may stabilize aerosol droplet size, reduce rate of knock down, stimulation of flight activity, prevention of deterioration of the toxicant, increased penetration into the insect, or formation of molecular complexes between synergist and insecticide[11-14]. In this study, we aimed to improve the toxic effect of the most active compounds (LC_{50} value < 100 ppm) against adult females of *T. urticae* by mixing with piperonyl butoxide in 1:2 ratio respectivelly.

The results in Table 5 indicate that piperonyl butoxide synergised all the tested compounds against the adult females of *T. urticae* (Koch.) and the highest synergistic acaricidal activity was obtained with 8-(*p*-chlorophenylsulfonate)quinoline (1f) and the percent of synergism was 110 %. Sulfonate derivatives were generally imporved by mixing with piperonyl butoxide more than thiosulfonate derivatives. Compound 1f (sulfonate derivatives) which has a chlorine atom at *p*-position of phenyl ring was the most active one compared to the other substituents followed by (1e) and (1b).

Synergistic effect of piperonyl butoxide to sulfonate and thiosulfonate derivatives against eggs of *T. urticae*: The mode of action of acaricides differ according to the form of stages ,i.e, moving stages or eggs. The effect on the eggs may be due to the degree of penetration

Table 5: Synergistic effect of piperonyl butoxide on the most potent sulfonate and thiosulfonate derivatives against adult females of *T. urticae*.

Compound	LC_{50} (ppm) alone	LC_{50} (ppm) with synergist	(S.R)	% of Synergism
Piperonyl butoxide	>1000	-	-	-
1b	27	17	1.65	65
1	85	49	1.72	72
1f	39	19	2.1	110
2a	85	60	1.42	42
2b	13	11	1.18	18
2c	23	20	1.17	17
2d	38	25	1.53	53
Propargite	68	-	-	-

Table 6: Synergistic ovicidal effect of piperonyl butoxide on sulfonate and thiosulfonate derivatives, against eggs of *T. urticae* (Koch.)

Compound	LC_{50} (ppm) alone	LC_{50} (ppm) with synergist	(S.R)[a]	% of Synergism
PB	>400	-	-	-
1a	669	59	11.24	1024
1b	743	86	8.63	763
1c	259	181	1.43	43
1d	289	38	7.52	652
1f	709	105	6.74	574
2a	149	39	3.82	282
2b	234	39	5.98	498
2c	286	46	6.19	519
2d	224	116	1.92	92
Propargite	100	-	-	-

rate through the shell, the vapor pressure of the tested compound, closing of respiratory pores which are present on the egg shell and/or effect on the hatching process or direct contact of larvae after hatching with the film of pesticides residue. There are many theories to investigate the mechanism of the ovicidal action of acaricides against eggs of mite and consequently, some compounds are ovicides or larvicides and some are only active as adulticides.

The obtained results of the synergistic effect of piperonyl butoxide on sulfonate and thiosulfonate are presented in Table 6. Comparing LC_{50} values of these compounds alone and after mixing with piperonyl butoxide indicate high reduction of the LC_{50} values showed an excellent synergistic effect with these derivatives against the eggs of *T. urticae* under laboratory conditions. The results of unsubstituted phenylsulfonate-1-yl naphthyl (compounds 1a-c) showed great synergisem by piperonyl butoxide at 1:2 ratio against the eggs (S.R = 11.24). Substitution with a methyl group on the phenyl ring as shown in compound 1b also showed high synergistic effect but it was less than the substitued one (S.R = 8.63). However, substitution with a chlorine atom on the phenyl ring (compound 1c) showed low synergistic effect compared to the other compounds in this group (S.R=1.43) .

The data of quinoline derivatives (1d and 1f) also indicate a good synergistic effect when mixed with PB at

1:2 ratio, respectively against the eggs of *T. urticae*. Unsubstituted phenyl ring as shown in compound 1d showed a higher synergistic ratio by piperonyl butoxide (S.R = 7.52) than that with the substituted phenyl ring with a chlorine atom as shown in compound 1f (S.R = 6.74).

Piperonyl butoxide has also synergized thiosulfonate compounds giving a good improvement in the ovicidal activity of *T. urticae* (Koch.) under laboratory conditions. A substitution with a chlorine atom as (compound 2c) was the most synergised one (S.R = 6.19). Moreover, replacing of chlorine with a methyl group as shown in compound 2b also gave a high effect against eggs (S.R = 5.98). Un-substituted phenyl ring (2a) was moderately activated (S.R = 3.82 compared to 2c and 2b derivatives.

Finally, synergistic effect of piperonyl butoxide on sulfonate and thiosulfonate derivatives dramaticaly improved the acaricidal activity against *T. urticae*. The LC_{50} of several derivatives including 2a-c, 1d and 1a. were highly reduced to be more effective than the standard acaricide propagite. These results are promising and of economical and practical importance for efficient control of *T. urticae* and could be improved in the near future.

REFERENCES

1. Badawy, M. E.I., 1997. Studies on the analysis of certain pesticide residues: Analysis and toxicity of certain acaricide and fungicide residues. M.Sc.Thesis, Faculty of Agriculture, Alexandria University..
2. Brown, A.W.A., 1956. Insect control by chemicals. John willy ans Sons. Inc. London, Chapman and Hall ltd. P: 817.
3. Dittrich, V., 1962. A comparative study of toxicological test methods on a population of the two-spotted spider mite (*Trtranychus telarius*). J. Econ. Entomol., 55: 644-648.
4. EL-Nawawy, A.S., A.H. El-Sebae and S.A. El-Khishin, 1963. Relation between chemical structure and biological activity. Part x.The insecticidal properties of some new isothiouronium organic salts. Alex. J. Agric. Res. XI (1): 189-198.
5. Finney, D.J., 1971. Probit analysis. 3rd Edn. Cambridge University press Cambridge, England.
6. Hewlett, P.S., 1960. Joint action in insecticides . Advances in Pest Control Research, Editted by R.L. Metcalf Vol. 3 Interscience Puplishers No.1.
7. Jee, Y.K.., H.S. Park, H.Y. Kim, J.S. Park, K.Y. Lee, K.Y. Kim, Y.K. Kim, S.H. Cho, K.U. Min and Y.Y. Kim, 2000. Two-spotted spider mite *Tetranychus urticae*: An important allergen in asthmatic non-farmers symtomatic in summer and fall months. Ann. Allergy. Asthma. Immunol. 84:543-548.
8. Kitagaki, T. and I. Hideo, 1974. Chloromethane esters sulfonate in acaricidal and fungicidal compositions for agricultural use. Kumiai Chemical Industry Co., Ltd. Japan 74 18, 208.
9. Kitagaki, T., S. Hironari and I. Hideo, 1973. Chloromethanesulfonate acaricides. *Kumiai Chemical Industry Co. Ltd. Japan.* 73 35,450.
10. Knowles, C.O., S. Ahmed and S.P. Shrivastava, 1972. Pesticide Chemistry, Vol. I (A.S. Tahori, ed.).Gordon and Breach, London, p: 77.
11. Maraei, A.S.M., A.S.A. Saad and G. Tantawy, 1971. Laboratory and field evaluation of certain pesticides against the adults and eggs of Tetranychus cinnabarinus (Boisduval) on cotton . J. Agric. Sci. Camb., 82: 391-394.
12. Metcalf, R.L., 1948. Acaricidal properties of organic compounds related to DDT. J . Econ. Entomol. 41: 875-882.
13. Metcalf, R.L., 1955. Organic insecticides, their chemistry and mode of action. Instersci. Publs., New York, pp: 792.
14. Metcalf, R.L., 1967. Mode of action of insecticide synergists. Ann. Revi. Entomo., 12: 229-256.
15. Navarro, A.M., J. Delgado, M.C. Sanchez; J.C. Orta, A. Martinez; R. Palacios, J. Martinez and J. Conde. 2000. Prevalence of sensitization to Tetranychus urticae in greenhouse workers. Clin. Exp. Allergy. 30: 863-866.
16. Siegler, E.H., 1947. Leaf-disk technique for laboratory tests of acaricides. J . Econ. Entomol. 40: 441-442.
17. Yoshinaga, E., W. Shigeki, D. Gosaburo and T. Kiyoshi, 1973a. p-Methylthiophenylvinylsulfonate as a pesticide. Kumiai Chemical Industry Co., Ltd.; Japan Kokai 73 82,030.
18. Yoshinaga, E., W. Shigeki, D. Gosaburo and T. Kiyoshi, 1973b. Pesticidal compositions containing phenyl-vinylsulfonate derivatives. Kumiai Chemical Industry Co., Ltd.; Japan Kokai, 73 77,022.