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Structure and Acaricidal Activity Relationship of Some Sulfonamide Derivatives Against the Two-spotted Spider Mite, *Tetranychus urticae* (Koch)

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ABSTRACT

Some of sulfonamide derivatives have been synthesized and their acaricidal activity against the two-spotted spider mite *Tetranychus urticae* (Koch) were evaluated. Morpholine sulfonamide derivatives were very potent against the adult and larval stage of *T. urticae*. In addition, the most active compounds were synergized by mixing with piperonyl butoxide (P.B) at the ratio of 1:2 to minimize the LC_{50} values and signaficant potency was obtained. The data indicated that morpholine sulfonamide derivatives (3a-c) could be promising to be developed in the future for controling *T. urtica*.

Key Words: Acaricidal activity; *Tetranychus urticae;* Sulfonamides; Structure-activity relationship; Two-spotted spider mite

INTRODUCTION

The two spotted spider mite, *Tetranychus urticae* Koch, is a serious pest of cotton, which is one of the most bedding plants in Egypt. It has been also recorded on more than 150 host plants of some economic value throughout the world (Jeppson *et al*., 1975). Most management tactics of mites rely upon application of pesticides (Smith & Mozingo, 1983; Brandenburg & Kennedy, 1987) such as pyrethroids, which are one of the most developed synthetic compounds. Moreover, continuous or repeated application of such pesticides, with the same mode of action have led to developing resistance among mite population (Helle & Sabelis, 1985; Young-Joon *et al*., 1993) and thus, increase in the frequency due to their toxicity to natural enemies. Furthermore, food contamination, mammalian toxicity and pollution of the environment are other problems that have to be recognized.

An important factor in *T. urticae* population resurgence is lack of toxicity to eggs and many of acaricides that are applied to the crop do not have good ovicidal properties. In this study, we synthesized and evaluated a series of sulfonamide derivatives against adult females and eggs of *T. urticae*. Also, the numbers of each life stage of *T. urticae* vary in a natural population and thus, it is important to know what and how the acaricide would be applied to mannage the *T. urticae* infestation in each life stage. Therefore, we extended our screening programme to determine both the ovicidal and larvicidal activity of such group of derivatives.

MATERIALS AND METHODS

General. Melting points were determined on a Kofler hot stage apparatus and were un-corrected. 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) and DMSO (dimethylsulfoxide) were used as solvents. *J* (coupling constant) values are given in Hz. Column chromatography was performed on (230 - 400 mesh) silica gel. All solvents were distilled and dried before use.

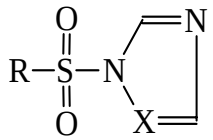
Synthesis

Synthesis of 1, 2, 4-triazole sulfonamide derivatives (1a-d). A weight of 1, 2, 4-triazole (0.01 mol, 0.69 g) in dichloromethane (20 mL) was stirred overnight with 0.01 mol of benzenesulfonylchloride (1a), *p*-tolunesulfonyl chloride (1b), *p*-chlorobenzenesulfonylchloride (1c) or methylsulfonylchloride (1d) in the presence of triethylamine (0.01 mol, 1.4 mL). The flask was fitted with a condenser and stirred overnight at room temperature. The mixture was poured in to a separatory funnel and washed with 100 mL distilled water. The organic layer was dried over anhydrous sodium sulfate (15 - 20 g) and the solvent was removed with a rotary evaporator. The residue was purified by flash chromatography and eluted by ethylacetate/hexane, 2: 3 to afford the desired compounds as solid crystals. The physiochemical properties and spectroscopic data are shown in Tables I and II, respectively.

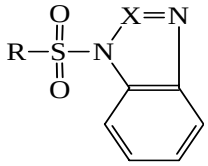
Synthesis of 1- (phenylsulfonamido)- imidazole derivatives (1e-g). Imidazole (0.01 mol, 0.68 g) was dissolved in dichloromethane (20 mL), then 0.01 mol of triethylamine was added at 0^{o}C to benzenesulfonylchloride (1e) or *p*-chlorobenzenesulfonylchloride (1f) or methylsulfonylchloride (1g). The flask was fitted with a condenser and stirred overnight at room temperature. The work-up has been carried out as described previuosely. The physiochemical properties and spectroscopic data are shown in Tables I and II, respectively.

Table I. Physiochemical properties of 1, 2, 4-triazole, imidazole, benzotriazole and benzimidazole sulfonamide derivatives

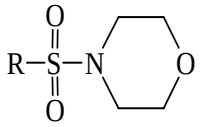
Compound	R	X	Yield (%)	m.p (°C)
1a	C_6H_5	N	63	128-130
1b	*p*-$CH_3C_6H_4$	N	84	95-97
1c	*p*-ClC_6H_4	N	68	189-190
1d	CH_3	N	47	84-85
1e	C_6H_5	C	64	75-76
1f	*p*-$CH_3C_6H_4$	C	65	77-78
1g	CH_3	C	47	189-190
2a	CH_3	N	54	109-110
2b	CH_3	C	47	198-200



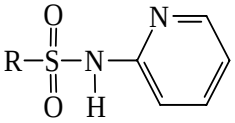
(1a-g)



(2a,b)



(3a-d)



(4a-c)

Synthesis of benzotriazol-1-yl methylsulfonamide (2a) and benzimidazole 1-methylsulfonamide (2b). Benzotriazole (in case of 2a) or benzimidazole (in case of 2b) 0.01 mol was dissolved in dichloromethane (20 mL) and stirred overnight with methylsulfonylchloride in the presence of a catalytic amount of triethylamine (0.01 mol, 1.4 mL) at 0°C. The flask was fitted with a condenser and stirred overnight at room temperature. The work-up has been carried out as previously described. Physiochemical properties and spectroscopic data are also shown in Tables I and II.

Synthesis of 1-(phenylsulfonamid)- morpholine derivatives (3a-d). A weight of morpholine (0.01 mol, 0.83 g) was dissolved in dichloromethane (20 mL), then triethylamine (0.01 mol, 1.40 mL) was added at 0°C in to 0.01 mol of benzenesulfonylchloride (3a) or *p*-toluenesulfonylchloride (3b) or *p*-chlorobenzene sulfonyl chloride (3c) or methylsulfonylchloride (3d) to prepare the desired compounds. The procedure was carried out as described previously. The physiochemical properties and spectroscopic data are shown in Tables III and IV, respectively.

Synthesis of 2-(phenylsulfonamido)-pyridine derivatives (4a-c). A weight of 2-aminopyridine (0.02 mol, 1.88 gm) was dissolved in dichloromethane (20 mL), then a catalytic amount (0.02 mol, 2.80 mL) of triethylamine was added at 0°C in to 0.02 mol of benzenesulfonyl chloride (4a) or *p*-chlorobenzenesulfonyl chloride (4b) or methylsulfonyl chloride (4c) to prepare the desired compounds (4a-c). The procedure and work-up was carried out as previously described. The physiochemical properties and spectroscopic data are shown in Tables III and IV.

Acaricidal Assay

Test animal. The infested cotton leaves were collected from the Agriculture Research Station of Alexandria University and transferred in to the laboratory. The adult females were selected by a fine hair brush (pelican brush No.000) to the castor leaves and maintained permanently in a glass rearing chamber (80 x 200 x 80 cm), which was covered with a wire net. Mites were always transferred from old leaves to new leaves. The colony was kept under laboratory conditions (25 ± 5°C, 60 - 70% relative humidity & 12 h daily illumination) (Badawy, 1997).

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%). Series of concentrations ranged from 10 to 1000 ppm were used.

Bioassay Techniques

Slide-dip technique (Adulticidal Screening). The method of Dittrich (1962) was used as follows: A piece of double faced scotch tape was pressed tightly to the surface of the slide. 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 the absorbent material for 15 min. The treated slides were put in to holding chamber at 27°C and about 95% relative humidity and kept horizontally. Mites were examined for mortality after 24 h of treatment under a microscope (10 x to 20 x). Mites, which failed to respond when prodded lightly

Table II. Spectroscopic data of 1, 2, 4-triazole sulfonamides (1a-d) benzotriazol-1-yl methylsulfonamide (2a) and benzimidazole (2b) derivatives

Entry	^{1}H-NMR (δ ppm)	IR (KBr) ν max cm^{-1}
1a	(*d*DMSO) 7.35 (3H, t, *J* = 6.8 Hz, Ph), 7.64 (2H, d, *J* = 7.2 Hz, Ph), 9.34 (2H, s, triazole)	1374, 1357, 1170
1b	(*d*DMSO) 2.3 (3H, s, CH_3), 7.15 (2H, d, *J* = 7.8 Hz, Ph), 7.54 (2H, d, *J* = 8.2 Hz, Ph), 9.11 (2H, s, triazole)	1388, 1268, 1200, 1178, 1142
1c	(*d*DMSO) 7.40 (2H, d, *J* = 8.4 Hz, Ph), 7.66 (2H, d, *J* = 8.4 Hz, Ph), 9.38 (2H, s, triazole)	1393, 1227, 1186, 1038
1d	(*d*DMSO) 2.50 (3H, s, CH_3), 9.42 (2H, s, triazole)	1377, 1183, 1045
1e	(*d*DMSO) 7.74 (5H, m, Ph), 8.11(2H, d, *J* = 8.2 Hz, imidazole), 8.42 (1H, s, imidazole)	1450, 1381, 1182, 1153
1f	(*d*DMSO) 7.41 (2H, d, *J* = 8.4 Hz, Ph), 7.64-7.70 (4H, m), 9.21 (1H, d, *J* = 29.6 Hz, imidazole)	1378, 1183, 1156, 1089
1g	(*d*DMSO) 2.45 (3H, s, CH_3), 7.69 (2H, s, imidazole), 9.1 (1H, s, imidazole)	1196, 1046, 781
2a	(*d*DMSO) 2.57 (3H, s, CH_3), 7.43 (2H, dd, *J* = 6.2 and 3.0 Hz, Ph), 7.92 (1H, dd, *J* = 6.2 and 3, Ph)	1390, 1361, 1142
2b	(*d*DMSO) 2.96 (3H, s, CH_3), 7.18 (2H, dd, *J* = 3.6 and 2.4 Hz, Ph), 7.43 (2H, dd, *J* = 3.8 and 2.2 Hz, Ph), 8.78 (1H, s, imidazole)	1396, 1370, 1324, 1154

Table III. Physiochemical properties of morpholine and 2-aminopyridine sulfonamide derivatives

Compound	R	Yield (%)	m.p (^oC)
3a	C_6H_5	86	176-178
3b	*p*-$CH_3C_6H_4$	79	165-167
3c	*p*-ClC_6H_4	81	140-141
3d	CH_3	47	87-88
4a	C_6H_5	57	178-180
4b	*p*-ClC_6H_4	71	198-200
4c	CH_3	68	189-190

with a fine brush were considered to be dead.

Leaf disc-dip method (Ovicidal & Larvicidal Screening). Discs of about 2 cm in diameter of castor leaves were used (Siegler, 1947). 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 h 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 un-treated controls in a holding chamber of about 25^{o}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 a synergist for most of the active compounds against adult and egg stages of *T. urticae* (Koch). Synergistic ratio (S.R) was calculated using Hewlett formula (1960).

Statistical analysis. LC_{50} (ppm) values with their fiducial limits for all treatments were determined by the probit-analysis method (Finney, 1971).

RESULTS AND DISCUSSION

Acaricidal activity of 1, 2, 4-triazol-1-yl and 1, 2, 3-benzotriazol-1yl sulfonamide derivatives. The results of triazole-1-yl-sulfone derivatives against adult females of *T. urticae* are shown in Table V. Compound 1c was the most active one in this group (LC_{50} = 87 ppm). Un-substituted phenyl ring showed moderate acaricidal activity compared to the standard acaricide, propargite. Substitution with chlorine on *p*-position of the phenyl ring dramatically enhanced the activity. However, replacing chlorine atom with methyl group decreased the activity. Also, replacing *p*-tolueyl with methyl group (1d versus 1b), decreased the activity. Comparing the activity of 1, 2, 4-triazole with 1, 2, 3-benzotriazole moiety indicated that there was no difference in their acaricidal activity (1d vesus 2a).

Acaricidal activity of imidazol-1-yl sulfonamide derivatives. The obtained results of these compounds are shown in Table V. Replacing one nitrogen atom of 1, 2, 4-triazole moeity with carbon atom gives imadazole. The un-substituted phenyl ring linked with imadazole showed low acaricidal activity compared to 1, 2, 4-triazole (1a versus 1e & 1d vesus 1g). Also, compound 2b, which contains benzaimidazole moiety showed lower effect against adult females of *T. urtica*e (LC_{50} > 1000 ppm). However, substitution with methyl group on *p*-position of phenyl ring as (1f; LC_{50} = 63) highly increased the activity (1f versus 1b) even up to the standared acaricide (LC_{50} = 68). Generally, replacing of phenyl ring with methyl group in all tested derivatives (1d, 1g, 2a & 2b) was un-successful to improve the acaricidal activity.

Acaricidal activity of morpholine sulfonamide derivatives. Morpholine moiety has shown certain biological activity against some pests (El-Zemity, 1996). Attempt for linking morpholine with sulfone was our approach to improve the pesticidal activity. The data in Table V showed that the un-substituted phenyl ring (3a) gave good acaricidal activity as much as the standard acaricide (propargite). Importantly, substitution with chlorine at *p*-position of the phenyl ring (3c) gave high acaricidal activity superior to the standard. Replacing chlorine with methyl group (compound 3b) slightly decreased the activity. Also replacing phenyl ring with methyl group (compound 3d) in all previous derivatives sharply reduced the acaricidal activity. The obtained data indicated types of compounds 3a-c could be promising and developed in the future for controlling adult females of *T. urtica*.

Acaricidal activity of 2-aminopyridine sulfonamide derivatives. The acaricidal activity of 2-aminopyridinylsulfone derivatives (Table V) against the adult females of *T. urticae* indicate that compound 4b (LC_{50}

Table IV. Spectroscopic data of 1-(phenylsulfonamido)morpholine derivatives (3a-d) and 2-(phenylsulfonamid)-pyridine derivatives (4a-c)

Entry	^{1}H-NMR (δ ppm)	IR (KBr) ν max cm^{-1}
3a	($CDCl_3$) 2.94 (4H, t, *J* = 4.8 Hz, morpholine), 3.68 (4H, t, *J* = 5 Hz, morpholine), 7.7 (2H, d, *J* =8.2 Hz, Ph), 7.55 (3H, t, *J* = 9.8 Hz, Ph)	1450, 1350, 1333, 1169, 1110
3b	($CDCl_3$) 2.38 (3H, s, CH_3), 2.92 (4H, t, *J* =4.8 Hz, morpholine), 3.67 (4H, t, *J* = 5 Hz, morpholine), 7.3 (2H, d, *J* = 8 Hz, Ph), 7.6 (2H, d, *J* = 8.4 Hz, Ph)	1346, 1165, 1113
3c	(*d*DMSO) 2.89 (4H, t, *J* = 4.8 Hz, morpholine), 3.65 (4H, t, *J* = 4.8 Hz, morpholine), 7.77 (4H, d, *J* = 9.2 Hz, Ph)	1349, 1261, 1165, 1110
3d	(*d*DMSO) 2.90 (3H, s, CH_3), 3.09 (4H, t, *J* = 4.8 Hz, morpholine), 3.67 (4H, t, *J* = 4.8 Hz, morpholine)	1325, 1261, 1160
4a	($CDCl_3$) 6.49 (1H, t, *J* = 7 Hz, Py), 7.0 (1H, d, *J* = 8.8 Hz, Py), 7.19 (3H, m, Ph),7.38 (1H, t , *J* = 9 Hz, Py), 7.60 (2H, d, *J* = 8 Hz, Ph), 7.78 (1H, d, *J* = 5.6Hz, Py), 12.40 (1H, br, NH)	2927, 2827 , 1629, 1391, 1356, 1283, 1143
4b	(*d*DMSO) 6.87 (1H, t, *J* = 6.8Hz, Py), 7.20 (1H, d, *J* = 8.8 Hz, Ph),7.61 (2H, d, *J* = 8.66 Hz, Ph), 7.77 (1H, t, *J* = 9 Hz, Py), 7.88 (2H, d, *J* = 8.6 Hz, Ph), 8.0 (1H, d, *J* = 5.6 Hz, Py), 12.45 (1H, br, NH)	2927, 2827, 1630, 1390, 1142
4c	(*d*DMSO) 3.26 (3H, s, CH_3), 7.0 (1H, t, *J* = 7.2 Hz, Ph), 7.03 (1H, d, *J* = 2.41, Py), 7.75 (1H, t, *J* = 8.2 Hz, Py), 8.21 (1H, d, *J* = 3.2 Hz, Py), 10.8 (1H, br, NH)	2928, 2817, 2760, 1391, 1362, 1291, 1270, 1122

= 56 ppm) was superior to the standared (LC_{50} = 68 ppm) proving that the presence of chlorine atom at *p*-position in all derivatives including 4b was very important in enhancing the acaricidal activity against adult females. But the un-substituted phenyl ring (compound 4a) as well as replacing the phenyl ring with methy group (4c) showed lower acaricidal activity compared to the standard.

Morpholine derivatives were the most active acaricides compared to the others except compound (3d). Imidazole and triazole derivatives indicated approximately the same activity against the adult females of *T. urticae* except compound 2b. Finally, we could conclude that the most potent compounds were the chlorine substituted sulfonamides derivatives in this study.

Ovicidal and larvicidal activity of 1, 2, 4- triazole and benzotriazole sulfonamide derivatives. The ovicidal, larvicidal and total kill percent of 1, 2, 4-triazol, (1a-d) and benzotriazole (2a) against *T. urticae* are shown in Table VI. All derivatives at concentration up to 1000 ppm were less active against eggs of *T. urticae*. However, better activity against larvae, particularly compound 1c at concentration reached 1000, was 83% mortality. Compounds 1d and 2a were moderately active as larvicides (44% & 49.78% mortality was obtained at 1000 ppm). Substitution at *p*-position of the phenyl ring with chlorine atom (compound 1c) enhanced the larvicidal activity. Generally, the un-substituted phenyl ring (1a) or substitution with methyl group on the phenyl ring (1b) did not differ in their toxicities. Besides, replacing the phenyl ring (1a) with a methyl group (1d) reduced the larvicidal activity.

Ovicidal and larvicidal activity of imidazole sulfonamide derivatives. Replacing 1, 2, 4-triazole (1a-1d) with imidazole (1e-1g) as in compound 1f, which is chlorine substituted at *p*-position of phenyl ring gave the highest ovicidal activity within this group at 1000 ppm (48% mortality; Table VII). However, results of larvicidal activity was much more important, where compound 1f gave 90% mortality followed by compound 1e (87%) at 1000 ppm. There was no difference in larvicidal activity between 1g (imidazole) and 2b (benzoimidazole). The descending order of activity as a total % kill against *T. urticae* was 1f (93%), 1e (89%), 2b (77%) and then compound 1g (72%) at 1000 ppm. The un-substituted phenyl ring (1e) showed better larvicidal activity than the ovicidal activity. In addition, replacing the phenyl ring with a methyl group (1e versus 1g & 2b) did not change the activity against eggs and its effect was reduced as larvicide.

Ovicidal and larvicidal activity of morpholine sulfonamide derivatives. This group of compounds showed slight activity against eggs, but it has a good effect against larvae of *T. urticae* (Table VII). Substituted phenyl ring with a chlorine atom or methyl group (compounds 3c & 3b) gave excellent activity as a total kill %. Also, *p*-Chlorophenylmorpholin-1-*yl*-sulfone (3c) was found to be very effective against the larvae with 78, 83 and 100% mortality at 100, 500 and 1000 ppm, respectively. However there was no clear difference in activity between compounds 3a and 3d regarding the total kill %.

Ovicidal and larvicidal activity of 2-amino pyridine sulfonamide derivatives. The results of 2-aminopyridylsulfone derivatives against eggs and larvae of

Table V. Acaricidal activity of 1, 2, 4-triazole, imidazole, morpholine and 2-aminopyridine sulfonamides derivatives against adult females of *T. urticae*

Compound	LC_{50} (ppm) after 24h.	95%fiducial limits	
		upper	lower
1a	103	199	53
1b	144	188	110
1c	87	128	59
1d	132	161	107
1e	133	178	99
1f	63	100	40
1g	148	176	125
2a	139	180	108
2b	> 1000	-	-
3a	68	109	43
3b	89	133	59
3c	50	57	43
3d	> 1000	-	-
4a	450	671	304
4b	56	82	38
4c	190	252	142
Propargite	68	78	59

Table VI. Ovicidal and larvicidal activity of 1, 2, 4-triazole and imidazole sulfonamide derivatives against *T. urticae*

Compound	Conc. (ppm)	Egg kill (%)	Larval kill (%)	Total kill (%)
	100	0.0	58	58
1a	500	4	63	64
	1000	6	74	76
	100	12	59	67
1b	500	15	64	70
	1000	4	74	75
	100	12	68	71
1c	500	12	74	77
	1000	0	84	83
	100	4	0	4
1d	500	4	31	34
	1000	3	44	46
	100	4	63	65
1e	500	19	74	79
	1000	9	87	89
	100	18	75	79
1f	500	26	81	84
	1000	48	90	93
	100	9	49	54
1g	500	3	52	53
	1000	25	63	72
	100	7	42	46
2a	500	0	0	0
	1000	19	50	59
	100	13	32	41
2b	500	15	46	54
	1000	36	65	77
	100	50	87	97
Propargite	500	100	-	100
	1000	100	-	100

T. urticae are summarized in Table VII. These compounds showed slight activity against larvae except 2-(phenylsulfonamido) pyridine (4a), which was the most active one (72% mortality at 1000 ppm). No ovicidal activity of this group was observed at the tested concentrations up to 1000 ppm.

Synergistic effect of piperony butoxide to certain sulfonamide derivatives against adult females of *T. urticae*. Synergists are usually of practical and economical importance in efficient control of pests. 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 was reported. Perhaps, they may stabilize aerosol droplet size, reduce rate of knockdown, stimulate flight activity, prevention of deterioration of the toxicant, increased penetration in to the insect, or formation of molecular complexes between synergist and insecticide (Metcalf, 1967). 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, respectively.

The synergism data of the most active compounds are shown in Table VIII. It was noticed that the synergism of imadazole (1f) was better than triazole (1c). Also, morpholine derivatives, which gave high acaricidal were considerably synergized to minimize the LC_{50} sharply particularly compound 3b (S.R = 3.75 & % of synergism = 275). However, piperonyl butoxide gave little synergism effect when mixed with either compounds 1c or 3c. Finally, it could be concluded that piperonyl butoxide gave the highest synergistic activity when mixed with sulfonamide derivatives than sulfonates and thiosulfonates against adult females of *T. urticae* (El-Zemity *et al.*, 2006). Besides, piperonyl butoxide is known as inhibitor of the mixed function oxidase (MFO) enzymes and thus, it will protect the insecticides from rapid detoxification.

Table VII. Ovicidal and larvicidal activity of morpholine and 2-aminopyridine sulfonamide derivatives against *T. urticae*

Compound	Conc. (ppm)	Egg kill (%)	Larval kill (%)	Total kill (%)
	100	18	19	34
3a	500	25	36	52
	1000	27	56	68
	100	3	67	68
3b	500	16	82	85
	1000	12	93	93
	100	13	78	81
3c	500	15	83	86
	1000	25	100	100
	100	8	38	43
3d	500	14	45	53
	1000	18	52	60
	100	11	68	69
4a	500	5	69	72
	1000	9	72	75
	100	20	17	34
4b	500	23	26	43
	1000	27	39	56
	100	8	28	34
4c	500	10	18	25
	1000	5	72	73
	100	50	87	98
Propargite	500	100	-	100
	1000	100	-	100

Table VIII. Synergistic effect of piperonyl butoxide to certain sulfonamide derivatives against adult females of *T. urticae*

Compound	LC_{50} (ppm) Alone	LC_{50} (ppm) with synergist	(S.R)	% of Synergism
PB	>1000	-	-	-
1c	87.19	60.96	1.43	43
1f	63.42	21.58	2.94	194
3a	68.43	30.99	2.21	121
3b	88.75	23.65	3.75	275
3c	49.74	35.16	1.41	41
4b	56.04	27.53	2.04	104
Propargite	68.00	-	-	-

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