Preparation of S-[2,3-bis(ethylthio)maleimidomethyl]thio- and -dithiophosphates, their spectral and biological properties

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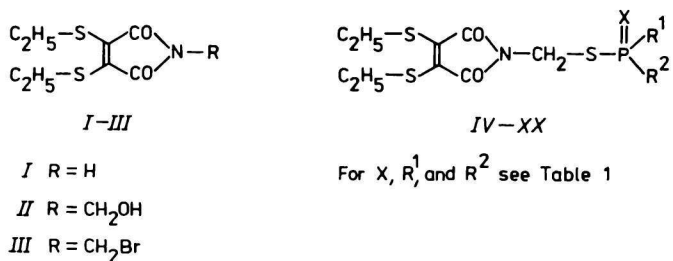ᵇResearch Institute of Agrochemical Technology,
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S-[2,3-bis(Ethylthio)maleimidomethyl]thio- and -dithiophosphates were prepared from N-bromomethyl-2,3-bis(ethylthio)maleimide and potassium salts of organophosphorus acids. Infrared, electronic, and in some cases also ¹H-n.m.r. spectra of the prepared compounds were measured. Linear relationship was found between $v(P=O)$ and $\Sigma\sigma^*$ of the substituents on phosphorus; the effect of medium on splitting of the absorption band $v(P=O)$ was studied. The prepared compounds were tested for insecticidal, acaricidal, ovicidal, and fungicidal activities.

Были приготовлены S-[2,3-бис(этилтио)малеинимидометил]тио- и -дитиофосфаты из N-бромметил-2,3-бис(этилтио)малеинимида и калиевых солей фосфорорганических кислот. Для приготовленных соединений были измерены инфракрасные и электронные спектры и для отдельных случаев также спектры ЯМР ¹H. Была найдена линейная зависимость между частотой $v(P=O)$ и $\Sigma\sigma^*$ заместителей на атоме фосфора и изучено влияние среды на расщепление полосы поглощения $v(P=O)$. Были определены инсектицидная, акарицидная, овицидная и фунгицидная эффективности приготовленных соединений.

This work deals with the synthesis of compounds structurally similar to the known insecticide "Imidan" (O,O-dimethyl S-phthalimidomethyl dithiophosphate), investigation of their pesticidal activities, and investigation of the effect of substituents on the wavenumber of the $v(P=O)$ stretching vibration in the infrared spectra [1—4].

The synthesis of S-[2,3-bis(ethylthio)maleimidomethyl]thio- and -dithiophosphates IV—XX (Table 1) was carried out from III (see Scheme 1).

C_2H_5-S ... CO ... $N-R$

$I-III$

$I \quad R = H$

$II \quad R = CH_2OH$

$III \quad R = CH_2Br$

C_2H_5-S ... CO ... $N-CH_2-S-\overset{\overset{X}{\|}}{P}\overset{R^1}{\underset{R^2}{}}$

$IV-XX$

For X, R^1, and R^2 see Table 1

Scheme 1

Experimental

˙ Infrared spectra of the prepared compounds in the region of 3000—500 cm^{-1} were measured on an IR-75 Zeiss spectrophotometer in tetrachloromethane. Absorption bands of the $v(P=O)$ stretching vibration in the region of 1300—1200 cm^{-1}, necessary for correlations, were measured on a UR-20 Zeiss spectrophotometer in tetrachloromethane, acetonitrile, and in the form of film so that the maxima of these absorption bands were ~75%. Measurements were performed in KBr cells of 0.127 mm thickness. The apparatus was calibrated by polystyrene foil. The wavenumbers of the absorption bands belonging to stretching vibration $v(P=O)$ were read with the accuracy of ± 1 cm^{-1}. The electronic spectrum of the compound *III* was measured in dioxan, the spectra of the other compounds in methanol on a Specord UV VIS (Zeiss, Jena) spectrophotometer in the range of 200—700 nm; the concentration of compounds was 5×10^{-5}—10^{-4} mol l^{-1}. ^{1}H-N.m.r. spectra were taken on a Tesla BS 487 A spectrophotometer (working frequency 80 MHz) at 25°C in deuteriochloroform using hexamethyldisiloxane as internal standard. Chemical shifts are given in δ relative to tetramethylsilane ($\delta_{HMDS} = 0.05$ p.p.m.).

The purity of the products was checked by thin-layer chromatography on Silufol UV 254 (Lachema, Brno) using the system ethyl acetate—benzene—cyclohexane (7 : 20 : 10).

Contact insecticidal activity was followed on *Musca domestica* L., *Calandra granaria* L., and *Aphis fabae* SCOP using Fenitrothion (*O,O*-dimethyl *O*-(3-methyl-4-nitrophenol) thiophosphate) as standard. Systemic insecticidal activity was followed on *Aphis fabae* SCOP using Thiometon (*O,O*-dimethyl *S*-(2-ethylthiomethyl) dithiophosphate) as standard. Acaricidal activity was followed on females of *Tetranychus urticae* KOCH, ovicidal activity on eggs of *T. urticae* using Karbofenthion (*O,O*-diethyl *S*-(4-chlorophenylthiomethyl) dithiophosphate) as standard. Insecticidal, acaricidal, and ovicidal activities were determined after [5, 6]. Fungicidal activity was determined by both the *in vitro* and *in vivo* methods. Inherent activity was followed on spores of *Sclerotinia fructicola* (WINT.) after the Sharvell method using Kaptan (3*a*,4,7,7*a*-tetrahydro-*N*-trichloromethanesulfenyl-phthalimide) as standard. Antipowdery mildew activity was followed by spraying the living plants of spring barley, sort Dunajský trh (*Erysiphe graminis* DC.) using Chloraniformethane [1-(3,4-dichloroaniline)-1-formylamido-2,2,2-trichloroethane] as standard, by spraying cucumbers (*Erysiphe polyphaga* HAMMARLUND) using Dinokap (2,4-dinitro-6-octylphenyl crotonate + 2,6-dinitro-4-octylphenyl crotonate) as standard, and by spraying tomatoes

(*Phytophoria infestans* De BY) using Mankozeb (Mn(II) and Zn(II) ethylenebisdithiocarbamates in the ratio of 7 : 1) as standard [7]. The activity on *Tilletia foetida, Botrytis cinerea,* and *Fusarium nivale* was determined after [8] by the zone method using Kaptan as standard. Systemic activity on *E. polyphaga* and *P. infestans* was determined by watering after [8] using Tridemorf (*N*-tridecyl-2,6-dimethylmorpholine) as standard.

N-Hydroxymethyl-2,3-bis(ethylthio)maleimide (II)

The mixture of 2,3-bis(ethylthio)maleimide (*I*) (70.0 g; 0.322 mol), 30% aqueous solution of formaldehyde (64.5 ml; 0.644 mol), and triethylamine (5 drops) was refluxed for 10 min under stirring. The orange oil was extracted into chloroform (200 ml) and washed with water. The organic layer was separated and dried over anhydrous sodium sulfate. After removing chloroform by distillation, 84 g (94%) of the compound *II*, a viscous yellow oil, was obtained; $n_D^{20} = 1.6010$, $R_f = 0.21$.

For $C_9H_{13}NO_3S_2$ (247.32) calculated: 43.71% C, 5.29% H; $\nu_s(CO)$ 1769, $\nu_{as}(CO)$ 1711, $\nu(C=C)$ 1513, $\nu(O—H)$ 3596; $\lambda(\varepsilon)$ 220 (8600), 259 (8600), 408 (5300); ^{1}H-n.m.r. δ (p.p.m.) (CH$_3$) 1.31, (CH$_2$—S) 3.30, (CH$_2$—N) 5.02, (O—H) 4.21.

N-Bromomethyl-2,3-bis(ethylthio)maleimide (III)

Into the solution of *N*-hydroxymethyl-2,3-bis(ethylthio)maleimide (*II*) (29.6 g; 0.12 mol) in dry benzene (60 ml) phosphorus tribromide (10.8 g; 0.04 mol) was added under stirring during 20 min so that the temperature of the reaction mixture did not rise above 30°C. Then the reaction mixture was boiled for 2 h under exclusion of atmospheric moisture. The benzene layer was decanted from phosphoric acid and benzene was distilled off. The orange oil was dissolved in chloroform (120 ml) and washed twice with glacial water (40 ml). The organic layer was separated, dried over anhydrous sodium sulfate, and filtered off. The solvent was distilled off under reduced pressure and the product, a viscous oil, was dried at 80°C and 26 Pa. On cooling the product solidified after some days; this was filtered off, washed with petroleum ether, and dried. Crystallization from the mixture of diethyl ether—pentane (1:1) gave the orange crystals of the compound *III* (27 g; 72%) of m.p. 52—54°C, $R_f = 0.58$.

For $C_9H_{12}NO_2S_2Br$ (310.22) calculated: 34.84% C, 4.51% N, 3.90% H; found: 34.70% C, 4.67% N, 3.80% H; $\nu_s(CO)$ 1765, $\nu_{as}(CO)$ 1723, $\nu(C=C)$ 1509; $\lambda(\varepsilon)$ 225 (5060), 255 (4400), 408 (2500); ^{1}H-n.m.r. δ(p.p.m.) (CH$_3$) 1.31, (CH$_2$—S) 3.36, (CH$_2$—Br) 5.30.

S-[2,3-bis(Ethylthio)maleimidomethyl]thio- (IV—XVII) and -dithiophosphates (XVIII—XX)

The mixture of *III* (4.7 g; 0.015 mol) and potassium salt of the appropriate organophos-

phorus acid (0.016 mol) was stirred for 20 min in butanone (20 ml) at 20—25°C. The reaction mixture was poured into concentrated aqueous solution of sodium chloride (150 ml) and shaken. The product was extracted with ethyl acetate or chloroform. The organic layer was separated and washed with water and the product was extracted with ethyl acetate. The organic layer was separated, dried over anhydrous sodium sulfate, and filtered. The solvent was distilled off under reduced pressure and the product, a viscous yellow oil, was dried at 80°C and 26 Pa.

The prepared compounds were purified by column chromatography on Silica gel L 40/100 (Lachema, Brno) using ethyl acetate—tetrachloromethane (1:1) as eluent.

Characterization of the prepared thiophosphates and dithiophosphates is presented in Table 1, infrared and electronic spectral data are in Tables 2 and 3.

Results and discussion

The starting compounds for the preparation of thiophosphates *IV—XVII* and dithiophosphates *XVIII—XX* (Table 1) were N-bromomethyl-2,3-bis(ethylthio)maleimide (*III*) and the appropriate salts of organophosphorus acids. Potassium salts of *O,O*-dialkyl phosphorothioic acids were prepared from the appropriate *O,O*-dialkyl phosphites [9]. Potassium salts of the other organophosphorus acids, necessary for the preparation of compounds *IV*, *V*, *XVI*, and *XVII*, were prepared by hydrolysis of chlorides of the appropriate organophosphorus acids with potassium hydroxide in aqueous dioxan [10]. Potassium salts of *O,O*-dialkyl phosphorodithioic acid were prepared from the appropriate *O,O*-dialkyl phosphorodithioic acids [11]. At the preparation of *III* we started from 2,3-bis(ethylthio)maleimide (*I*) [12]. By hydroxymethylation of *I* with formaldehyde under catalysis of triethylamine [13] we prepared N-hydroxymethyl-2,3-bis(ethylthio)maleimide (*II*). Employing the procedure after [14], we prepared N-bromomethyl-2,3-·bis(ethylthio)maleimide (*III*) from *II* by treatment with phosphorus tribromide. The components of the reaction mixture, checked by thin-layer chromatography, indicated that the reaction of *III* with salts of organophosphorus acids (Scheme 1) proceeded with high yields already at room temperature and reaction time 15—20 min; this was found also in paper [4].

The electronic spectra of the prepared esters of organophosphorus acids (*IV—XX*) (Table 2) differed very little from the electronic spectrum of the starting compound *III*. With regard to the reactivity of the compound *III* towards nucleophilic reagents, its spectrum was measured in dioxan instead of methanol.

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In the i.r. spectra of esters of organophosphorus acids (*IV—XX*) (Table 2) an intensive absorption band belonging to stretching vibration of v(PO-alkyl) was observed in the region of 1025—976 cm^{-1} [15, 16]. The intensive band at 943 cm^{-1} observed with the compound *IV* and the band of medium intensity at 935 cm^{-1} with the compound *V* belonged to stretching vibration of v(PO-aryl) [16]. In the region of stretching v(CO) vibration two absorption bands were observed with all compounds prepared. The more intense band at lower wavenumbers 1723—1708 cm^{-1} was attributed to asymmetric and the less intense one at higher wavenumbers 1770—1761 cm^{-1} to symmetric vibrations of the dicarbonyl system [17]. The band of low intensity at 1515—1509 cm^{-1} belonged to stretching vibration of v(C=C). The wavenumber of this band is, approximately, by 30 cm^{-1} lower than that of the v(C=C) of structurally similar compounds containing 5,6-dihydro-1,4-dithiin ring [18]. The band of medium intensity at 653—649 cm^{-1} belonging to stretching vibration of v(P=S) was characteristic of dithiophosphates *XVIII—XX* [15] and the band of medium intensity at 1280—1230 cm^{-1} belonging to stretching vibration of v(P=O) was characteristic of thiophosphates *IV—XVII* (Table 3) [19]. The absorption band belonging to stretching v(P=O) vibration of the prepared compounds (*IV—XVII*, Table 3) measured in tetrachloromethane was a doublet and the distance between the maxima of these absorption bands $v_2 - v_1$ (in cm^{-1}) decreased with the decreasing sum of the Taft σ^* constants of the substituents R^1 and R^2. With the compounds *XVI* and *XVII* (Table 3) having the lowest values of $\Sigma \sigma^*$ only one absorption band belonging to v(P=O) was present or the doublet was not distinguishable anymore. The difference in the wavenumbers $v_2 - v_1$ corresponds to the difference reported for doublets of v(P=O) in the literature [19]. In acetonitrile as well as in the original form of a film this absorption band was not split and the wavenumber v(P=O) with the individual thiophosphates corresponded to the arithmetic mean of the wavenumbers v_1 and v_2. We came to analogous conclusions in our preceding paper [4] with the series of thiophosphates. The fact that the wavenumber of the absorption band v(P=O) correlates with the sum of the Taft σ^* constants of the substituents [20] was found to be valid also with the prepared thiophosphates (*IV—IX, XVI, XVII*). Statistical parameters of correlations are presented in Table 4. Into the $\Sigma \sigma^*$ we included only two substituents R^1 and R^2 on phosphorus as the Taft σ^* constant of the third substituent, bound on phosphorus *via* sulfur, was unknown. We have not included the compounds *X—XV* into the correlation between the wavenumber v(P=O) and $\Sigma \sigma^*$ because $\sigma^*(R^1) + \sigma^*(R^2)$ of the alkoxy groups of these compounds was practically constant and the wavenumber v(P=O) did not change either. The Taft σ^* constants of the substituents were taken from the works [3, 21—23]. The structures of the starting compounds (*II, III*) as well as of some esters of organophosphorus acids (*VI—VIII, XVIII*) were proved also by ^{1}H-n.m.r. spectral data (Table 5). The signals of protons in the groupings P—S—C—H and

Table 1

Characteristics of the prepared organophosphorus compounds

Compound	X	R^1	R^2	Formula	M	Calculated/found		Yield %	n_D^{20}	R_t
						% C	% H			
IV	O	C$_6$H$_5$O	C$_6$H$_5$O	C$_{21}$H$_{22}$NO$_5$PS$_3$	495.56	50.89	4.47	88	1.6202	0.45
						50.54	4.52			
V	O	C$_6$H$_5$O	C$_2$H$_5$O	C$_{17}$H$_{22}$NO$_5$PS$_3$	447.56	45.62	4.95	85	1.5665	0.30
						45.89	4.68			
VI	O	CH$_3$O	CH$_3$O	C$_{11}$H$_{18}$NO$_5$PS$_3$	371.41	35.50	4.88	89	1.5797	0.09
						35.32	4.74			
VII	O	C$_2$H$_5$O	C$_2$H$_5$O	C$_{13}$H$_{22}$NO$_5$PS$_3$	399.47	39.06	5.55	94	1.5654	0.12
						39.28	5.44			
VIII	O	n-C$_3$H$_7$O	n-C$_3$H$_7$O	C$_{15}$H$_{26}$NO$_5$PS$_3$	427.52	42.14	6.13	87	1.5555	0.21
						41.91	6.01			
IX	O	n-C$_4$H$_9$O	n-C$_4$H$_9$O	C$_{17}$H$_{30}$NO$_5$PS$_3$	455.57	44.80	6.63	81	1.5454	0.29
						44.51	6.41			
X	O	n-C$_5$H$_{11}$O	n-C$_5$H$_{11}$O	C$_{19}$H$_{34}$NO$_5$PS$_3$	483.62	47.18	7.08	90	1.5432	0.37
						47.28	7.19			
XI	O	n-C$_6$H$_{13}$O	n-C$_6$H$_{13}$O	C$_{21}$H$_{38}$NO$_5$PS$_3$	511.67	49.32	7.42	84	1.5340	0.41
						49.09	7.24			
XII	O	n-C$_7$H$_{15}$O	n-C$_7$H$_{15}$O	C$_{23}$H$_{42}$NO$_5$PS$_3$	539.72	51.18	7.84	91	1.5266	0.46
						51.29	7.72			
XIII	O	n-C$_8$H$_{17}$O	n-C$_8$H$_{17}$O	C$_{25}$H$_{46}$NO$_5$PS$_3$	567.77	52.88	8.16	88	1.5232	0.50
						52.62	8.11			
XIV	O	n-C$_9$H$_{19}$O	n-C$_9$H$_{19}$O	C$_{27}$H$_{50}$NO$_5$PS$_3$	395.82	54.42	8.46	92	1.5221	0.53
						54.30	8.19			
XV	O	n-C$_{10}$H$_{21}$O	n-C$_{10}$H$_{21}$O	C$_{29}$H$_{54}$NO$_5$PS$_3$	623.87	55.83	8.72	84	1.5196	0.57
						55.65	8.63			

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Table 1 (Continued)

Compound	X	R¹	R²	Formula	M	Calculated/found		Yield %	n_D^{20}	R_f
						% C	% H			
XVI	O	C_2H_5O	C_6H_5	$C_{17}H_{22}NO_4PS_3$	431.56	47.31	5.14	89	1.5745	0.13
						46.99	5.16			
XVII	O	CH_3O	$(CH_3)_2N$	$C_{12}H_{21}N_2O_4PS_3$	384.50	37.49	5.51	80	1.5559	0.05
						37.70	5.40			
XVIII	S	CH_3O	CH_3O	$C_{11}H_{18}NO_4PS_4$	387.53	34.12	4.68	93	1.6137	0.59
						34.19	4.61			
XIX	S	C_2H_5O	C_2H_5O	$C_{13}H_{22}NO_4PS_4$	415.89	37.55	5.34	96	1.5964	0.65
						37.39	5.20			
XX	S	$n\text{-}C_8H_{17}O$	$n\text{-}C_8H_{17}O$	$C_{25}H_{46}NO_4PS_4$	583.92	51.42	7.94	95	1.5467	0.79
						51.70	7.78			

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Table 2

Infrared ($\bar{\nu}/cm^{-1}$) and electronic spectral data of the organophosphorus compounds

Compound	$\nu_s(CO)$	$\nu_{as}(CO)$	$\nu(C=C)$	$\nu(PO-C)$	$\nu(P=S)$	λ_{max}/nm	$(\varepsilon_{max}\cdot 10^{-3}/l\ mol^{-1}\ cm^{-1})$	
IV	1770	1720	1513	943	—	211 (21.8)	264 (7.8)	418 (4.7)
V	1770	1719	1513	935 1026	—	213 (11.0)	265 (8.0)	416 (4.7)
VI	1769	1718	1513	1025	—	214 (9.7)	266 (7.5)	416 (5.0)
VII	1769	1718	1514	976 1021	—	215 (8.6)	266 (7.5)	413 (4.8)
VIII	1768	1717	1513	1001	—	213 (8.5)	267 (7.1)	416 (4.0)
IX	1765	1715	1511	985 1055	—	213 (9.6)	266 (7.2)	415 (4.7)
X	1768	1717	1513	990	—	214 (9.5)	263 (7.4)	415 (4.8)
XI	1770	1720	1515	998	—	216 (9.7)	266 (7.4)	413 (4.8)
XII	1770	1719	1513	1002	—	214 (9.1)	267 (7.1)	416 (4.6)
XIII	1776	1715	1513	998	—	213 (9.2)	266 (7.0)	418 (4.7)
XIV	1765	1713	1511	995	—	212 (10.2)	266 (7.5)	418 (4.9)
XV	1768	1716	1513	993	—	214 (10.4)	261 (7.5)	415 (4.7)
XVI	1767	1717	1511	953 1023	—	213 (17.8)	266 (8.0)	415 (4.4)
XVII	1761	1708	1510	1025	—	210 (9.4)	266 (7.0)	413 (4.2)
XVIII*	1767	1717	1513	1021	653	214 (12.4)	269 (6.4)	416 (4.6)
XIX*	1765	1715	1513	955 1013	649	212 (13.9)	270 (7.0)	416 (5.0)
XX*	1763	1712	1513	1021	652	213 (12.4)	269 (6.8)	416 (4.8)

Table 3

Wavenumbers $\nu(P=O)$ of thiophosphates and σ^* constants of the substituents

Compound	$\nu(P=O)^a$	$\nu(P=O)^b$	$\nu_1(P=O)^c$	$\nu_2(P=O)^c$	$\nu(P=O)^d$	$\nu_2 - \nu_1$	$\Sigma\sigma^{*e}$
IV	1273	1276	1265	1287	1276.0	22	4.48
V	1265	1267	1258	1277	1267.0	19	3.88
VI	1262	1264	1254	1270	1262.0	16	3.46
VII	1256	1257	1250	1264	1257.0	14	3.28
VIII	1255	1258	1249	1264	1256.5	15	3.14
IX	1254	1259	1248	1263	1255.5	15	3.10
X	1254	1259	1250	1264	1257.0	14	—
XI	1254	1259	1253	1263	1268.0	10	—
XII	1255	1260	1252	1264	1258.0	12	—
XIII	1256	1260	1253	1264	1258.5	11	—
XIV	1255	1261	1250	1264	1257.0	14	—
XV	1256	1260	1251	1264	1257.5	13	—
XVI	1233	1233	1239	—	—	—	2.35
XVII	1232	1234	1236	—	—	—	2.26

a) Measured in acetonitrile; *b)* measured in original state in the form of film; *c)* measured in tetrachloromethane; *d)* arithmetic mean wavenumbers $\nu_1(P=O)$ and $\nu_2(P=O)$; *e)* $\Sigma\sigma^* = \sigma^*$ (R^1) + σ^* (R^2).

Table 4

Statistical parameters of the linear correlation between
$\nu(P=O)$ and $\Sigma\sigma^*$ with thiophosphates *IV—IX, XVI, XVII*

$\nu(P=O)$	r	ϱ	s_ϱ	q	s_q	s
$\nu(P=O)^a$	0.972	19.21	6.61	1191.4	5.8	3.40
$\nu(P=O)^b$	0.890	18.24	1.62	1200.8	11.2	6.31
$\nu_1(P=O)^c$	0.995	12.20	0.76	1210.6	1.9	0.64
$\nu_2(P=O)^c$	0.994	17.76	1.21	1207.7	3.0	1.01
$\nu(P=O)^d$	0.990	17.98	3.73	1197.8	3.3	7.60

r — correlation coefficient; ϱ — slope; s_ϱ — standard deviation ϱ; q — intercept on the axis of wavenumbers; s_q — standard deviation q; s — residual scattering.
For *a—d* see Table 3.

P—N—C—H were split by the nucleus of phosphorus and the interaction constant was in the interval of 14—16 Hz. This finding was supported by the observation that the signals of methylene group in the grouping N—CH$_2$—OH (with the compound *II*) and in the grouping N—CH$_2$—Br (with the compound *III*) were singlets.

Table 5

'H-NMR spectral data of the organophosphorus compounds

Compound	Group	δ/p.p.m.	$^3J_{P-O-C-H}$ Hz	$^3J_{P-N-C-H}$ Hz
VI	CH₃—CH₂—S	1.33 (6H, t)	14.7	15.1
	CH₃—CH₂—S	3.34 (4H, q)		
	CH₃—O	3.78 (6H, d)		
	N—CH₂	4.88 (2H, d)		
VII	CH₃—CH₂—S	1.33 (6H, t)	—	14.9
	CH₃—CH₂—S	3.34 (4H, q)		
	CH₃—CH₂—O	1.36 (6H, t)		
	CH₃—CH₂—O	4.17 (4H, m)		
	N—CH₂	4.88 (2H, d)		
VIII	CH₃—CH₂—S	1.33 (6H, t)	—	14.8
	CH₃—CH₂—S	3.33 (4H, q)		
	CH₃—CH₂—CH₂—O	0.96 (6H, m)		
	CH₃—CH₂—CH₂—O	1.60 (4H, m)		
	CH₃—CH₂—CH₂—O	3.96 (4H, m)		
	N—CH₂	4.69 (2H, d)		
XVIII	CH₃—CH₂—S	1.34 (6H, t)	15.7	14.6
	CH₃—CH₂—S	3.33 (4H, q)		
	CH₃—O	3.81 (6H, d)		
	N—CH₂	4.87 (2H, d)		

s — singlet; d — doublet; t — triplet; q — quadruplet; m — multiplet.

Table 6

Acaricidal and ovicidal activities (LD_{50} in p.p.m.) of some organophosphorus compounds

Compound	*Tetranychus urticae* KOCH	
	Females	Eggs
VI	12	—
VII	8	—
VIII	1020	—
IX.	1020	—
XVIII	15	—
XIX	25	300
Imidan	15	0.1
Karbofenthion	0.59	44.0

The contact insecticidal activity on *M. domestica, C. granaria*, and *A. fabae* in concentration $100 \rightarrow 5000$ p.p.m. was low, not comparable with the used standard.

Similar results were obtained in systemic insecticidal activity on *A. fabae*. The highest acaricidal and ovicidal activities were observed on *T. urticae*. The compounds *VI*, *VII*, *XVIII*, and *XIX* (Table 6) displayed the highest activity. In tests for fungicidal activity measurable values were observed only with the compound *VI*.

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