ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN – POLONIA

VOL. LXI, 14 SECTIO AA 2006

Syntheses and properties of novel 1-[2-(polyhalogenophenoxy)acyl]-3,5-dimethyl-1H-pyrazole

B. Tarasiuk
Department of Organic Chemistry and Technology
Faculty of Chemistry, Maria Curie-Skłodowska University
ul. Gliniana 33, 20-614 Lublin, Poland

The results of the study on the syntheses and properties of new 3,5-dimethyl-1*H*-pyrazole derivatives of 2-[polychloro- (bromo)phenoxy]alkane acids are presented. The compounds were synthesised during the reaction of 2-(polyhalogenoaryloxy)alkanoic chlorides with an on 3,5-dimethylpyrazole and N,N-diethylaniline. The compounds are characterized by means of FTIR, ^{1}H NMR and ^{13}C NMR spectrum using a nuclear magnetic resonance spectrometer, and elemental analysis. Their physical-chemical properties were examined, along with their fungicidal, insecticidal, acaricidal and herbicidal activity. It was found that he highest herbicidal activity characterised the derivatives of 1-(2,4-dichlorophenoxyacetyl)-3,5-dimethyl-1*H*-pyrazole, 1-[2-(2,4-dichlorophenoxy)propanoyl]-3,5-dimethyl-1*H*-pyrazole, 1-(2,4,5-trichlorophenoxyacetyl)-3,5-dimethyl-1*H*-pyrazole and 1-[2-(2,4,5-trichlorophe-noxy)propanoyl]-3,5-dimethyl-1*H*-pyrazole.

1. INTRODUCTION

Derivatives of phenoxy acids show a high biological activity. Especially the salts of those acids were widely applied in many areas of agriculture, among the others as herbicides, fungicides and regulators of the plant growth [1-3]. The chemical properties of these herbicides are due to the aromatic radical (phenyl) and the presence of the carboxyl group [4].

The physiological activity of phenoxyacetic acid increases when a halogen such as fluorine or chlorine is introduced into the aromatic radical, the position of the halogen is being very important. For example, in the dichlorophenoxyacetic acid series, 2,4-dichlorophenoxyacetic acid has the

highest physiological activity. When one hydrogen atom is substituted by an aliphatic hydrocarbon radical in a molecule of a phenoxyacetic acid, the activity of the compound grows insignificantly.

Esters and other derivatives of the halogenphenoxyalkane acids have a more pronounced herbicidal activity, which is explained by their better ability of penetrating through the epidermal tissues of plants, and first of all through the cuticle [1,4,6].

In sensitive plants, the action of herbicides that are phenoxyalkane acid derivatives manifests itself quite rapidly. Already in a few hours, growth is inhibited or completely stopped, the petioles and young shoots curl, and the entire plant bends abnormally. Thickenings are formed in the lower parts of plants from which adventitious roots appear. The upper parts of roots thicken and decay, and young roots die off.

In plants treated with herbicides, the intensity of respiration first grows, then the process of photosynthesis is inhibited as a result of decomposition of the chlorophyll and the stopping of its biosynthesis. Hydrolytic decomposition of starch, insulin, and proteins occurs, and the processes of synthesis stop [1, 4-6].

To reach the final scope it is necessary to use definitely smaller doses of esters than those of their salts are or free acids. Actual task for the researchers who carry out the investigation on the pesticides is to receive the new derivatives of the aryloxyalkane acids of more biological activity at the diminished dose of the preparation, used on a mass scale to protect the industrial cultivation.

In the Department of Organic Chemistry and Technology investigation has been carried out for many years in order to look for some new organic compounds of potential biological activity [7-16]. Lately, it has concentrated on the research related to the synthesis of 3,5-dimethyl-1*H*-pyrazole derivatives of 2-[polychloro-, (bromo)-phenoxy]alkane acids.

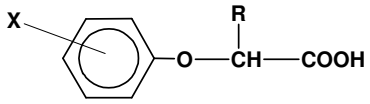
2. EXPERIMENTAL

Materials. 2,4-Dichlorophenol (mp = 42–43ºC), 3,4-dichlorophenol (mp = 66–68ºC), 2,5-dichlorophenol (mp = 56–58ºC), 3,5-dichlorophenol (mp = 67–68ºC), 2,4-dibromophenol (mp = 40–42ºC), 2,4,6-trichlorophenol (mp = 64–66ºC), 2,4,5-trichlorophenol (mp = 67–69ºC), 2,4,6-tribromophenol (mp = 92–94ºC), pentachlorophenol (mp = 188–191ºC), ethyl chloroacetate (bp = 143ºC), ethyl 2-chloropropionate (bp = 146–149ºC), thionyl chloride (bp = 79ºC) and 3,5-dimethyl-1*H*-pyrazole (mp = 107–109ºC), all from Aldrich, Germany.

Synthesis of 2-(polyhalogenoaryloxy)acetic (propionic) acids. At first, a convenient method was elaborated to synthesise the 2-(polychloro-,

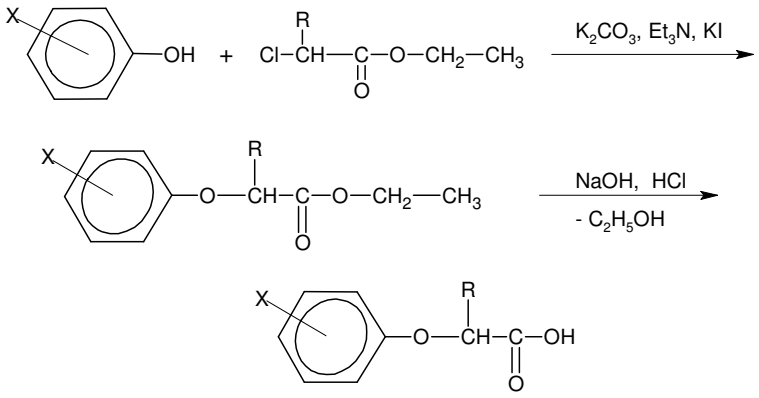
bromophenoxy)acetic (-propionic) acids. Starting with suitable polychloro- or polybromophenols and ethyl chloroacetate or ethyl 2-chloropropionate in presence of potassium carbonate, tributylamine and potassium iodide and cyklohexanone as solvent, at the temperature of 85 ºC during 15 hours one received, at high yield the esters of the corresponding 2-(aryloxy)acetic (propionic) acids. After the separation and purification, they were hydrolysed for 2 hours in a water ethanol solution of sodium hydroxide at the temperature of 80ºC. Free acids were separated from the reaction mixture by adding a 10% water solution of hydrochloric acid. Raw acids were purified by crystallisation from ethanol. The data concerning the structure of these acids, melting point was presented in Table 1.

Tab. 1. Melting points of 2-(polyhalogenoaryloxy)acetic -(propionic) acids.



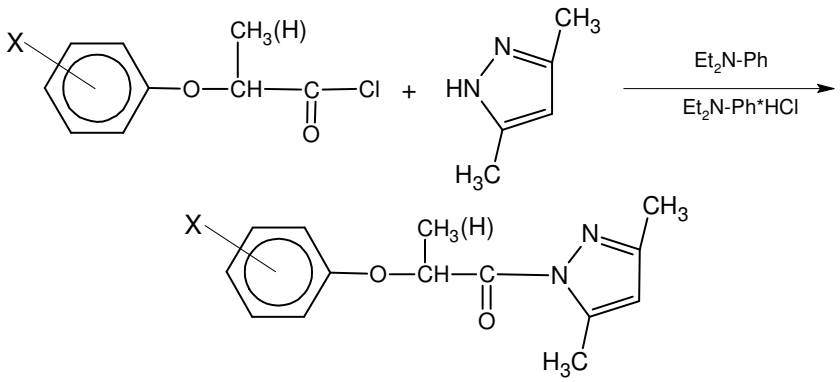
Comp. no.	Substituent		Melting point [°C]	Melting point [°C] acc. literature
	R	X		
1	H	2,4-Cl_2	140-141	141 [6]
2	CH_3	2,4-Cl_2	116-118	117-118 [6]
3	H	2,5-Cl_2	147-149	142-143 [3]
4	CH_3	2,5-Cl_2	137-138	136.5-137.5 [20]
5	H	3,4-Cl_2	140-141	141 [3]
6	CH_3	3,4-Cl_2	120-122	119.8-121.2 [19]
7	H	3,5-Cl_2	117-118.5	117.5-118 [18]
8	CH_3	3,5-Cl_2	144-145.5	144-145.5 [9]
9	H	2,4-Br_2	150-152	152 [2]
10	CH_3	2,4-Br_2	141-142	140-141.5 [21]
11	H	2,4,6-Cl_3	182-183	177 [2]
12	CH_3	2,4,6-Cl_3	125-126	125-126 [22]
13	H	2,4,5-Cl_3	159-160	158-159 [6]
14	CH_3	2,4,5-Cl_3	180-181	179-181 [6]
15	H	2,4,6-Br_3	199-200	200 [23]
16	CH_3	2,4,6-Br_3	131-132	130-131.5 [23]
17	H	Cl_5	194-196	195-196 [1]

The course of reaction that produced the 2-(polychloro- bromophenoxy)acetic (propionic) acids was represented in the general scheme:



X = 2,4-Cl_2, 3,4-Cl_2, 2,5-Cl_2, 3,4-Cl_2, 2,4-Br_2, 2,4,6-Cl_3, 2,4,5-Cl_3, 2,4,6-Br_3 and Cl_5
R = H or CH_3

The chlorides of 2-aryloxyalkane acids were received in the reaction of the acids with an excess of thionyl chloride. 1-[2-(Aryloxy)acyl]-3,5-dimethylpyrazole were synthesised in reaction of corresponding acid chlorides with an excess of 3,5-dimethylpyrazole and diethylaniline in benzene. The course of reaction that poduced the derivatives in question was represented in a general scheme:



X = 2,4-Cl_2, 3,4-Cl_2, 2,5-Cl_2, 3,5-Cl_2, 2,4-Br_2, 2,4,6-Cl_3, 2,4,5-Cl_3, 2,4,6-Br_3 and Cl_5

Synthesis of 1-[2-(polyhalogenoaryloxy)acyl]-3,5-dimethyl-1H-pyrazole. In a round bottom three-necked flask of 250 cm^3, equipped with a mechanical stirrer, a thermometer, 2.9 g (0.03 mol) of 3,5-dimethyl-1*H*-pyrazole, 50 cm^3 of dry benzene and 6.7 g (0,045 mol) N,N-diethylaniline was placed. While stirring the contents of the flask, a solution of 0.02 mole of a corresponding 2-(aryloxy)acid

chloride was dropped into it in 100 cm^3 of dry benzene, during 30 minutes, keeping the temperature within the range of 12-16 ºC. While carrying out the reaction a colourless, fine crystals sediment of diethylaniline hydrochloride started to set out. After the whole amount of acid chloride was introduced into the reaction mixture, the whole of it was still stirred during 2 hours at a temperature of 30–35ºC. The sediment of diethylaniline hydrochloride were filtered and washed with dry warm benzene. Then the solution was concentrated under diminished pressure while heating on the boiling water bath, and, after it was cooled down to the temperature of 5ºC, the crystals were carefully filtered. The raw compound was purified by crystallisation from a mixture of ethanol and cyclohexane or heptane.

The yield of the reaction was determined, the melting temperature of the synthesized derivatives, and their solubility in water, acetone and ethanol (in 100 cm^3 of temperature 25 ºC). In order to confirm the structure of the studied compounds, an elemental analysis was carried out as well as the FTIR analysis (apparatus: spectrophotometer Perkin Elmer model 1725X; KBr) and spectroscopy of ^{1}H NMR and ^{13}C NMR (apparatus: spectrometer Broker Avance 300, 300 MHz; $CDCl_3$).

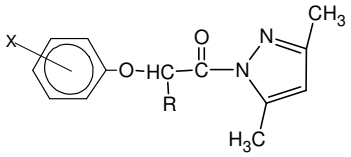
Newly obtained compounds were investigated at the Institute of Organic Industry in Warsaw with regard to their biological activity. The physiological activity of compounds mentioned above was studied against the insect, the *Tetranychus urticae* Koch, some plants and fungi [17].

The studies of insecticidal activity were carried out in the laboratory, using some bioindicators, such as *Musca domestica* and *Tetranychus urticae* Koch. In the investigations, a sample of 0.1% acetone solution of the inestigated compounds in the case of *Tetranychus urticae* Koch, and 25 μg for *Musca domestica* were used after 48 hours the morality test of the bioindicators had been carried out. The fungicidal activity was studied *in vitro*, using the fungi: *Alternalia tenures*, *Botrytis cinerea, Rhizoctonia solani, Fusarium culmorum* on living plants covered with the spores of *Erysiphe graminis*. The phytocidal reaction of the compounds was studied before germination and after germination on 10 selected indicative plants, using the concentration corresponding to a dose of 5 kg/hectare. The investigated compounds did not show any insecticide activity, neither the *Musca domestica* nor *Tetranychus urticae* Koch.

3. RESULTS AND DISCUSSION

New organic compounds were received, of the type 3,5-dimethyl-1*H*-pyrazole derivative of 2-[polychloro- (bromo)phenoxy]alkane acids. The data concerning the structure of these compounds, the yield of reaction, melting point and their solubility in three basic solvents were presented in Tables 2 and 3.

Tab. 2. Structure of 1-[2-(polyhalogenoaryloxy)acyl]-3,5-dimethyl-1*H*-pyrazole.



Comp. no.	Substituent		Formula	Molecular mass
	R	X		
1	H	2,4-Cl_2	$C_{13}H_{12}Cl_2N_2O_2$	299.16
2	CH_3	2,4-Cl_2	$C_{14}H_{14}Cl_2N_2O_2$	313.19
3	H	2,5-Cl_2	$C_{13}H_{12}Cl_2N_2O_2$	299.16
4	CH_3	2,5-Cl_2	$C_{14}H_{14}Cl_2N_2O_2$	313.19
5	H	3,4-Cl_2	$C_{13}H_{12}Cl_2N_2O_2$	299.16
6	CH_3	3,4-Cl_2	$C_{14}H_{14}Cl_2N_2O_2$	313.19
7	H	3,5-Cl_2	$C_{13}H_{12}Cl_2N_2O_2$	299.16
8	CH_3	3,5-Cl_2	$C_{14}H_{14}Cl_2N_2O_2$	313.19
9	H	2,4-Br_2	$C_{13}H_{12}Br_2N_2O_2$	388.06
10	CH_3	2,4-Br_2	$C_{14}H_{14}Br_2N_2O_2$	402.09
11	H	2,4,6-Cl_3	$C_{13}H_{11}Cl_3N_2O_2$	333.61
12	CH_3	2,4,6-Cl_3	$C_{14}H_{13}Cl_3N_2O_2$	347.64
13	H	2,4,5-Cl_3	$C_{13}H_{11}Cl_3N_2O_2$	333.61
14	CH_3	2,4,5-Cl_3	$C_{14}H_{13}Cl_3N_2O_2$	347.64
15	H	2,4,6-Br_3	$C_{13}H_{11}Br_3N_2O_2$	466.75
16	CH_3	2,4,6-Br_3	$C_{14}H_{13}Br_3N_2O_2$	480.98
17	H	Cl_5	$C_{13}H_9Cl_5N_2O_2$	402.50

The structure of the synthesised molecules of 1-[2-(aryloxy)acyl)-3,5-dimethyl-1*H*-pyrazole confirms a very good agreement of the results of elemental analysis and the calculated contents of the atoms of C, H, N (Tab. 4) and the presence of the characteristic peaks of the absorption bands in the spectres in Fourier transform infrared spectrophotometer (Fig. 1 and Tab. 5) and the values of nuclear magnetic resonance spectrometer (Tables 6 and 7).

Important absorption peaks observed in the 1-[2-(aryloxy)acyl)-3,5-dimethyl-1*H*-pyrazoles spectra included the peaks (Fig. 1) corresponding to the carbonyl group at 1733–1737 cm^{-1}, stretching vibration of H-C in phenyl ring peak at 3018–3076 cm^{-1}, CH, CH_2, CH_3 stretching vibrations at 2920–2987 cm^{-1}, stretching vibrations of the C=C and C=N in aromatic ring at 1484–1650 cm^{-1}, and stretching vibrations of the Ph-O-C $_{sym., asym.}$ at 1250 cm^{-1} and 1045 cm^{-1}.

Tab. 3. Yield of reaction, melting point and solubility of 1-[2-(aryloxy)acyl]-3,5-dimethyl-1*H*-pyrazole.

Comp. no.	Yield [wt. %]	M. p. [°C]	Solubility [g/100 cm^3]		
			Acetone	Ethanol	Water
1	61	135-137	12	3.5	0.1
2	89	110-112	19	4.5	0.2
3	88	127-129	10	1.5	-
4	85	112-113	16	2.0	-
5	79	101-102	17	4.5	-
6	71	72-74	20	5.0	-
7	88	101-102	13	2.5	
8	82	86-87.5	17	3.5	
9	80	141-143	10	3.0	-
10	83	120-121	12	3.5	-
11	80	129-131	11	2.3	0.05
12	85	111-112	17	1.1	0.1
13	88	133-134	10	2.1	-
14	79	171-172	11	2.5	-
15	79	123-124	8	2.5	-
16	87	97-98	7	3.0	-
17	91	128-130	4	1.5	-

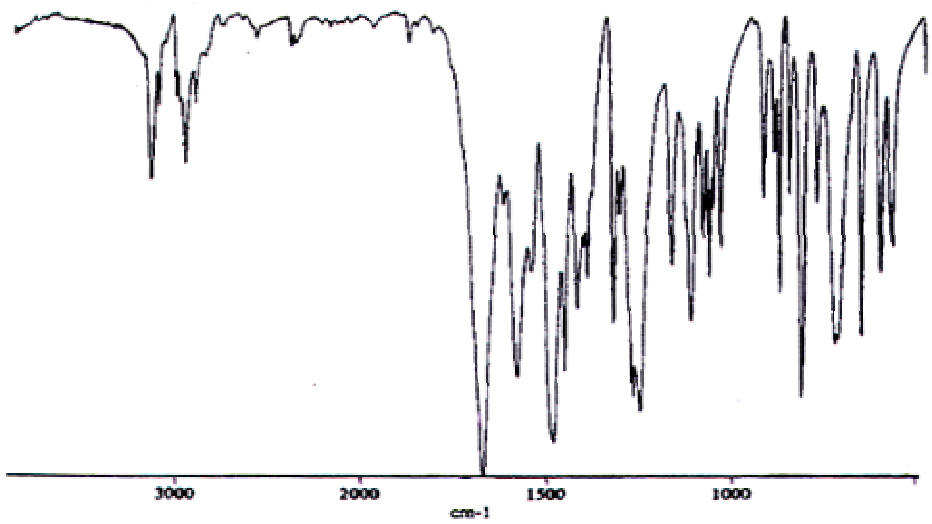


Fig. 1. FTIR spectra of 1-[2-(2,4-dichlorophenoxy)propanoyl]-3,5-dimethyl-1*H*-pyrazole.

Tab. 4. The results of elemental analysis of 1-[2-(polyhalogenoaryloxy)acyl]-3,5-dimethyl-1*H*-pyrazole.

Comp.	Calculated [wt.%]			Found [wt.%]		
no.	C	H	N	C	H	N
1	52.19	4.04	9.36	52.27	4.13	9.40
2	53.69	4.51	8.94	53.64	4.58	8.87
3	52.19	4.04	9.36	52.07	4.01	9.41
4	53.69	4.51	8.94	53.58	4.62	9.13
5	52.19	4.04	9.36	52.23	4.15	9.30
6	53.69	4.51	8.94	53.80	4.39	8.98
7	52.19	4.04	9.36	52.22	4.01	9.40
8	53.69	4.51	8.94	53.47	4.55	9.01
9	40.24	3.12	7.22	40.33	3.09	7.21
10	41.82	3.51	6.97	41.90	3.49	7.03
11	46.80	3.32	8.40	46.88	3.37	8.49
12	48.37	3.77	8.06	48.42	3.71	8.03
13	46.80	3.32	8.40	46.77	3.30	8.44
14	48.37	3.77	8.06	48.29	3.80	8.10
15	33.45	2.38	6.00	33.53	2.43	5.98
16	34.96	2.72	5.82	35.01	2.80	5.80
17	38.79	2.25	6.96	38.83	2.30	6.98

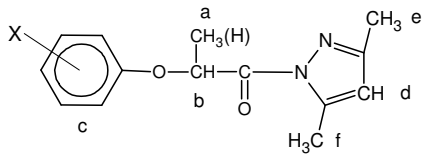
Tab. 5. FTIR spectral data (υ_{max}/cm) for 1-[2-(aryloxy)acyl]-3,5-dimethyl-1*H*-pyrazole.

No	H-C=C_{Ph}	CH_3,CH_2,CH	C=O	Ph -O- CH	C=C_{Ph}
1	3075, 3020	2989, 2964, 2924	1736	1252, 1045	1650, 1584, 1486
2	3075, 3020	2982, 2963, 2923	1735	1251, 1045	1650, 1584, 1486
3	3075, 3020	2981, 2965, 2922	1732	1251, 1045	1650, 1584, 1486
4	3075, 3020	2989, 2965, 2922	1734	1250, 1045	1650, 1585, 1486
5	3075, 3020	2989, 2964, 2925	1735	1253, 1046	1651, 1583,1485
6	3075, 3021	2985, 2964, 2923	1735	1252, 1044	1650, 1585, 1487
7	3075, 3022	2987, 2967,2923	1734	1251, 1046	1650, 1586, 1487
8	3076, 3022	2987, 2966, 2924	1734	1251, 1045	1650, 1585, 1486
9	3075, 3021	2987, 2967, 2920	1735	1251, 1045	1650, 1586, 1486
10	3075, 3021	2986, 2965, 2926	1734	1250, 1045	1650, 1585, 1486
11	3075, 3020	2987, 2965, 2920	1734	1252, 1043	1650, 1585, 1484
12	3075, 3018	2988, 2966, 2927	1734	1250, 1048	1650, 1586, 1487
13	3075, 3018	2986, 2967, 2927	1734	1250, 1043	1650, 1586, 1487
14	3075, 3018	2987, 2964, 2926	1735	1250, 1043	1650, 1586, 1487
15	3075, 3018	2984, 2966, 2925	1736	1250, 1044	1650, 1586, 1487
16	3075, 3018	2988, 2965, 2928	1734	1250, 1046	1650, 1586, 1487
17	3075, 3018	2986, 2965, 2926	1734	1250, 1046	1650, 1585, 1487

In the ^{1}H NMR spectrum of 1-[2-(aryloxy)acyl)-3,5-dimethyl-1*H*-pyrazoles, all signal corresponding to the proposed structure were observed in $CDCl_3$. Assignments of the chemical shifts are as follows: 1.7-1.8 ppm (doublet, methyl

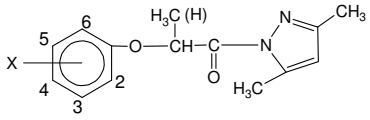
protons), 2.2 and 2.6 ppm (double singlet, methyl protons in pyrazole ring), 5.8-5.9 ppm (singlet, PhO-$\underline{C}H_2$-CO), 6.1 ppm (multiplet, PhO-C$\underline{H}(CH_3)$-CO), and 5.9-6.0 ppm (singlet, proton in pyrazole ring). The signals corresponding to aromatic protons could be observed at 6.80-7.82 ppm.

Tab. 6. ^{1}H-NMR spectral data (σ/ppm) for 1-[2-(aryloxy)acyl]-3,5-dimethyl-1*H*-pyrazole.



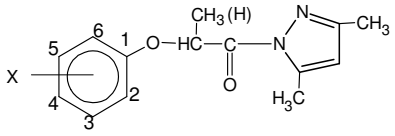
Comp. no.	C$\underline{H}_3$-CH-O a	C=C-C$\underline{H}_3$ f	N=C-C$\underline{H}_3$ e	O-C$\underline{H}_2$- B	O-C$\underline{H}$-CH$_3$ b C=C-$\underline{H}$ d	Ph- $\underline{H}$ c
1	-	s; 2.2; 3xH	s; 2.6; 3xH	s; 5.8 2xH	s; 6.1; 1xH	d; 6.7-7.2 4xH
2	d;1.7; 3xH J=6.6 Hz	s; 2.2; 3xH	s; 2.6; 3xH	-	m; 5.9-6.0; 2xH	m; 6.8-7.2 4xH
3	-	s; 2.2; 3xH	s; 2.6; 3xH	s; 5.9 2xH	s; 6.1; 1xH	m; 6.7-7.1 9xH
4	d;1.7; 3xH J=6.6 Hz	s; 2.2; 3xH	s; 2.6; 3xH	-	m; 5.9-6.1; 2xH	m; 6.7-7.1 9xH
5	-	s; 2.2; 3xH	s; 2.6; 3xH	s; 5.9 2xH	s; 6.1; 1xH	m; 7.0-7.6 4xH
6	d;1.8; 3xH J=6.6 Hz	s; 2.2; 3xH	s; 2.6; 3xH	-	m; 5.9-6.1; 2xH	m; 7.0-7.5 4xH
7	-	s; 2.2; 3xH	s; 2.6; 3xH	s; 5.9 2xH	s; 6.1; 1xH	m; 7.0-7.6 4xH
8	d;1.8; 3xH J=6.6 Hz	s; 2.2; 3xH	s; 2.6; 3xH	-	m; 5.9-6.1; 2xH	m; 7.0-7.5 4xH
9	-	s; 2.2; 3xH	s; 2.6; 3xH	s; 5.9 2xH	s; 6.1; 1xH	m; 7.0-7.6 4xH
10	d;1.8; 3xH J=6.6 Hz	s; 2.2; 3xH	s; 2.5; 3xH	-	m; 5.9-6.1; 2xH	m; 7.2-7.6 4xH
11	-	s; 2.2; 3xH	s; 2.6; 3xH	s; 5.9 2xH	s; 6.1; 1xH	m; 7.2-7.6 3xH
12	d;1.8; 3xH J=68 Hz	s; 2.2; 3xH	s; 2.5; 3xH	-	m; 5.9-6.1; 2xH	m; 7.2-7.6 3xH
13	-	s; 2.2; 3xH	s; 2.6; 3xH	s; 5.9 2xH	s; 6.1; 1xH	m; 7.2-7.6 3xH
14	d;1.7; 3xH J=6.6 Hz	s; 2.2; 3xH	s; 2.5; 3xH	-	m; 5.9-6.1; 2xH	m; 7.2-7.6 3xH
15	-	s; 2.2; 3xH	s; 2.6; 3xH	s; 5.9 2xH	s; 6.1; 1xH	m; 7.2-7.6 3xH
16	d;1.8; 3xH J=6.6 Hz	s; 2.2; 3xH	s; 2.6; 3xH	-	m; 5.9-6.1; 2xH	m; 7.2 -7.6 3xH
17	-	s; 2.2; 3xH	s; 2.5; 3xH	s; 5.9 2xH	s; 6.1; 1xH	s; 7.5 2xH

Tab. 7. ^{1}H-NMR spectral data (σ/ppm) for phenyl rings of 1-[2-(aryloxy)acyl]-3,5-dimethyl-1*H*-pyrazole.



Comp. no.	X	H-C$_2$	H-C$_3$	H-C$_4$	H-C$_5$	H-C$_6$
1	2,4-Cl$_2$	-	d; 7.38 J_m=2.5Hz	-	d,d; 7.16 J_o=8.8Hz; J_m=2.5Hz	d; 6.92 J_o=8.8Hz
2	2,4-Cl$_2$	-	d; 7.32 J_m=2.5Hz	-	d,d; 7.17 J_o=8.8Hz J_m=2.5Hz	d; 6.94 J_o=8.8Hz
3	2,5-Cl$_2$	-	d; 7.41 J_o=8.5Hz	d,d; 6.99 J_o=8.5Hz J_m=2.3Hz	-	d; 7.11 J_m=2.3Hz
4	2,5-Cl$_2$	-	d; 7.41 J_o=8.5Hz	d,d; 6.99 J_o=8.5Hz J_m=2.3Hz	-	d; 7.11 J_m=2.3Hz
5	3,4-Cl$_2$	d; 6.97 J_m=2.8Hz	-	-	d; 7.34 J_o=8.8Hz	d,d; 6.75 J_o=8.8Hz J_m=2.8Hz
6	3,4-Cl$_2$	d; 6.99 J_m=2.8Hz	-	-	d; 7.33 J_o=8.8Hz	d,d; 6.74 J_o=8.8Hz J_m=2.8Hz
7	3,5-Cl$_2$	d; 6.80 J_m=2.5Hz	-	d; 6.99 J_m=2.5Hz	-	d; 6.80 J_m=2.5Hz
8	3,5-Cl$_2$	d; 6.81 J_m=2.5Hz	-	d; 6.98 J_m=2.5Hz	-	d; 6.81 J_m=2.5Hz
9	2,4-Br$_2$	-	d; 7.55 J_m=2.5Hz	-	d,d; 7.37 J_o=8.8Hz J_m=2.5Hz	d; 6.68 J_o=8.8Hz
10	2,4-Br$_2$	-	d; 7.56 J_m=2.5Hz	-	d,d; 7.36 J_o=8.8Hz J_m=2.5Hz	d; 6.69 J_o=8.8Hz
11	2,4,6-Cl$_3$	-	d; 7.19 J_m=2.5Hz	-	d; 7.19 J_m=2.5Hz	-
12	2,4,6-Cl$_3$	-	d; 7.18 J_m=2.5Hz	-	d; 7.18 J_m=2.5Hz	-
13	2,4,5-Cl$_3$	-	s; 7.16	-	-	s; 6.74
14	2,4,5-Cl$_3$	-	s; 7.15	-	-	s; 6.74
15	2,4,6-Br$_3$	-	d; 7.59 J_m=2.5Hz	-	d; 7.59 J_m=2.5Hz	-
16	2,4,6-Br$_3$	-	d; 7.60 J_m=2.5Hz	-	d;7.60 J_m=2.5Hz	-
17	Cl$_5$	-	-	-	-	-

Tab. 8. ^{13}C NMR spectral data (σ/ppm) for phenyl rings of 1-[2-(aryloxy)acyl]-3,5-dimethyl-1*H*-pyrazole.



Comp. no.	X	C_1	C_2	C_3	C_4	C_5	C_6
1	2,4-Cl_2	152.0	123.5	130.2	126.9	127.8	114.4
2	2,4-Cl_2	151.4	124.3	130.3	127.1	127.9	115.3
3	2,5-Cl_2	154.5	120.0	130.8	121.2	132.1	114.2
4	2,5-Cl_2	154.0	120.2	130.8	121.8	132.4	114.9
5	3,4-Cl_2	156.6	117.0	132.1	125.2	131.1	114.0
6	3,4-Cl_2	156.1	117.0	132.8	125.1	131.0	114.5
7	3,5-Cl_2	155.9	114.8	133.9	121.2	137.3	111.1
8	3,5-Cl_2	155.8	114.8	133.8	121.2	137.5	111.3
9	2,4-Br_2	154.5	112.6	134.1	117.3	132.1	116.0
10	2,4-Br_2	155.1	112.6	134.6	117.3	132.1	115.8
11	2,4,6-Cl_3	152.1	125.1	128.4	129.3	128.7	121.4
12	2,4,6-Cl_3	152.1	125.1	128.4	129.3	128.7	121.4
13	2,4,5-Cl_3	153.0	121.9	131.6	128.4	134.5	115.6
14	2,4,5-Cl_3	153.0	121.9	131.6	128.4	134.5	115.6
15	2,4,6-Br_3	159.0	115.3	135.1	119.5	135.1	115.3
16	2,4,6-Br_3	159.0	115.3	135.1	119.5	135.1	115.3
17	Cl_5	155.2	123.6	135.9	130.1	136.2	120.0

In the ^{13}C NMR spectrum of 1-[2-(aryloxy)acyl)-3,5-dimethyl-1*H*-pyrazoles in chloroforme-d_1 signals were observed at 16.3, 19.4, 20.8, 68.4, 77.5, 129.9, 137.4, 163.9 and 169.1 ppm, which were attributable to methyl groups on Ph-O-CH(<u>C</u>H_3)-CO and the pyrazole ring, the Ph-O-<u>C</u>H_2-CO carbon, Ph-O-<u>C</u>H(CH_3)-CO, on aromatic carbons on the pyrazole rings, and the carbonyl carbon, respectively. The signals corresponding to phenyl carbons could be observed at 112-159 ppm.

The discussed organic compounds are colourless substances of melting temperature 72-172ºC. In the volume of 100 cm^3 of solvent at temperature 25ºC they dissolve in 1.5-5.0 g in ethanol, 4.0–19.0 g in acetone and in trace amounts in water (Table 3). These compounds, while having a considerable large molecule, and so a large molecular weight (some 299-480 g/mole) characterise with a considerable solubility in acetone and ethanol.

Tab. 9. Phytocidal activity of 1-[2-(polyhalogenoaryloxy)acyl]- 3,5-dimethyl-1*H*-pyrazole in of screening test.

	Compound no.						
Bio indicator	**1**	**2**	**3**	**4**	**13**	**14**	**17**
Lolium perenne L –	3*	3	1	1	3	4	2
Lp	1**	1	0	1	1	2	0
Avena sativa L –	3	3	1	2	3	4	2
As	1	1	0	1	1	3	0
Zea mays L –	2	3	1	1	3	3	3
Zm	1	1	0	1	1	3	1
Sinapis alba L –	4	4	0	3	3	3	2
Sa	2	2	1	1	3	3	1
Pisum sativum L –	4	4	1	2	4	4	2
Ps	3	3	0	1	3	4	2
Phaseolus vulgaris L - Phv	4	4	1	2	2	3	2
	1	2	0	1	2	2	2
Cucumis sativus L –	4	4	1	1	3	2	1
Cs	1	2	1	1	2	2	2
Linum usitatissimum L – Lu	3	3	1	2	3	3	2
	2	2	1	1	3	1	1
Beta vulgaris L –	3	3	1	1	4	3	2
Bv	2	2	0	1	1	2	1
Fagopyrum esculentum	2	2	0	1	3	2	1
Moench - FeM	1	1	0	0	1	0	1

Application: (*) pre emergency, (**) post emergency.
Phytotoxicity: rating scale ranged from 0 to 4
(0 – no injury, 4 – complete death plant) [17].

Biological screening results. The 3,5-dimethyl-1*H*-pyrazole derivatives of the 2-(aryloxy)alkane acids showed no insecticidal or acaricidal activity. The compounds showed only a medium fungicidal potency against *Erysiphe graminis*, and the level of biological activity was no sufficient for further interest, so they were eliminated from test. The most interesting activity was noticed in primary phytocidal screen using ten plant bio indicators.

The primary data are presented in Table 7 and Figures 2 and 3. The compounds no 5, 6, 7, 8, 9, 10, 11, 12, 15 and 16 show insignificant biological activity. The highest phytocidal activity was largely confined to the compounds No. 1, 2, 3, 4, 13, 14 and 17. They were selected for evaluation in the secondary screen for herbicidal activity. The results confirmed good herbicidal activity for most of them. All chemicals caused symptoms similar to those produced by phenoxyalkane acids class of herbicides after pre emergence and post emergence applications. The best compounds: 1-(2,4-dichloro-phenoxyacetyl)-3,5-dimethyl-1*H*-pyrazole, 1-[2-(2,4-dichlorophenoxy)propanoyl]-3,5-dimethyl-1*H*-pyrazole,

1-(2,4,5-trichlorophenoxyacetyl)-3,5-dimethyl-1*H*-pyrazole, 1-[2-(2,4,5-trichlorophenoxy)propanoyl]-3,5-dimethyl-1*H*-pyrazole (derivatives No. 1, 2, 13 and 14). good controlled *dicotyledonous* weed species at the dose 2.5 and 1.25 kg a.i./ ha.

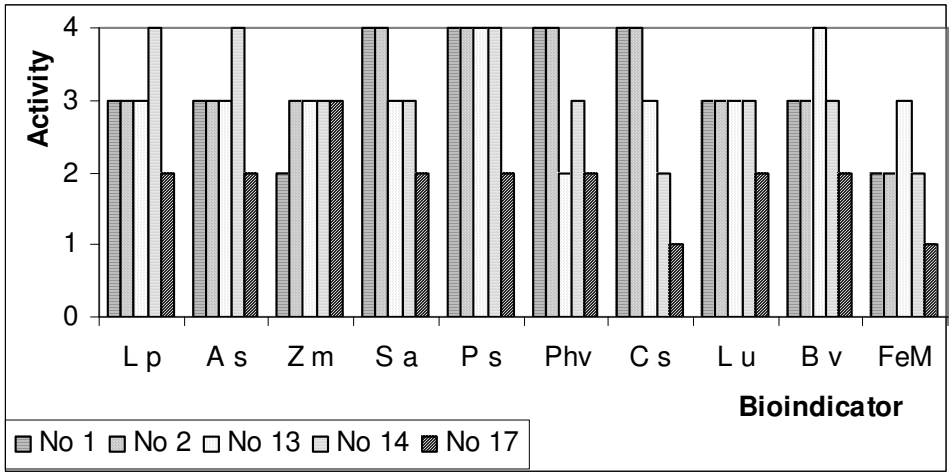


Fig. 2. Phytocidal activity of the 1-[2-(polyhalogenoaryloxy)acyl]- 3,5-dimethyl-1*H*-pyrazole in pre emergence application.

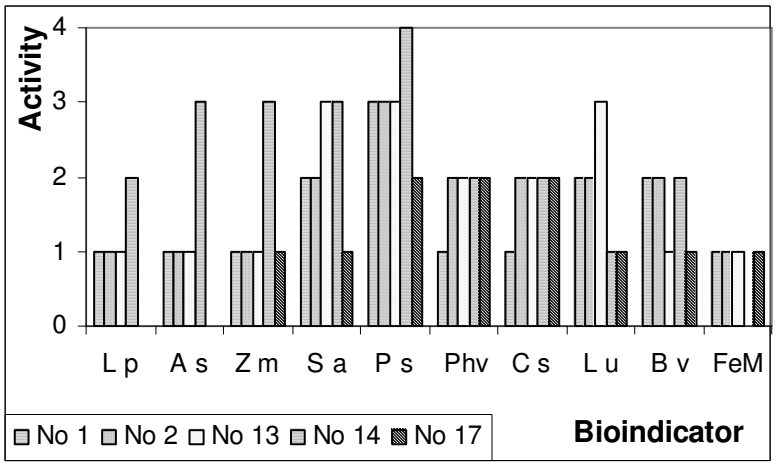


Fig. 3. Phytocidal activity of the 1-[2-(polyhalogenoaryloxy)acyl]- 3,5-dimethyl-1*H*-pyrazole in post emergence application.

Herbicidal activity of this compound was studied under the field condition in the 3-rd stage of screening-test and promising results was obtained. The further investigation was stopped because of technological problems and rather high price of semi-products during derivatives synthesis.

Additionally the series of biological activity tests was conducted to compare the following compounds: 1-[2-(2,4-dichlorophenoxy)propanoyl]-3,5-dimethyl-1*H*-pyrazole, 2-(2,4-dichlorophenoxy)propane acid and 3,5-dimethyl-1*H*-pyrazole 2-(2,4-dichlorophenoxy)propionate. The most active compound against *dicotyledons* weed species being the 3,5-dimethyl-1*H*-pyrazole derivative of 2-(dichlorophenoxy)propionic acid, next the salt and free acid, but 3,5-dimethyl-1*H*-pyrazole showed no herbicidal activity.

In summary, the 3,5-dimethyl-1*H*-pyrazole derivatives of 2-(polyhalogenophenoxy)alkane acids showed good herbicidal activity at pre emergence and post emergence application.

4. REFERENCES

[1] M. E. Synerholm and P. W. Zimmerman, *Contrib. Boyce Thompson Inst*., 14, 91 (1945)
[2] L. Haskelberg, *J. Org. Chem*., 12, 426 (1947)
[3] H. R. Lewis, J. R. Housley, H. C. Richards, J. S. Nicholson, M. W. Bakes, S. S. Adams, *Pat. Brit*., 916,242 (1963), Chem. Abstr. 59, 5080^c (1963)
[4] G. S. Gruzdyev et al., *The Chemical Protection of Plants,* G.S. Gruzdyev (ed). Mir Publishers, Moscow 1988, p.364
[5] A. Fredga, *Arkiv. Kemi,* 18, 501 (1962)
[6] N. N. Melnikow, *Pesticide,* K.W. Nowozyw (ed). Khimiya., Moscow 1987, p.226
[7] W. Podkościelny, B. Tarasiuk, Z. Zimińska, *Przem. Chem.,* 73, 466 (1994)
[8] E. Bakuniak et al., *Pestycydy*, 1, 21 (1993)
[9] B. Tarasiuk, *Pestycydy*, 1, 5 (1996)
[10] B. Tarasiuk, W. Podkościelny, *Przem. Chem.,* 74, 250 (1995)
[11] B. Tarasiuk, W. Podkościelny, Z. Zimińska, M. Krawczyk, *Pestycydy*, 1, 5 (2000)
[12] B. Tarasiuk, W. Podkościelny, *Annales UMCS, Sectio AA,* LVI(19), 283 (2001)
[13] B. Tarasiuk, *Annals of the Polish Chemical Society*, 2, 75 (2003)
[14] B. Tarasiuk, *Annales UMCS, Sectio AA,* LIX(8), 77 (2004)
[15] M. Janicka, B. Ościk-Mendyk, B. Tarasiuk, *Journal of Planar Chromatography – Modern TLC*, 17(3), 186 (2004)
[16] B. Tarasiuk, *Annals of the Polish Chemical Society,* 4, 187 (2005)
[17] E. Bakuniak et al., *Pestycydy,* 4, 12 (1978)
[18] J. C. Newman et al. *J. Amer. Chem. Soc.,* 69, 718 (1947)
[19] M. S. Matell, *Arkiv. Kemi.,* 4, 473 (1952)
[20] A. Fredga, *Croat. Chem. Acta*; 29, 313 (1957)
[21] A. Grabowska et al., *Rocz. Chem.*; 43, 715 (1969)
[22] M. S. Matell; *Arkiv. Kemi*, 9, 157 (1956)
[23] J. Toothill et al.; *Ann. Appl. Biol.,* 44, 547 (1956)

CURRICULUM VITAE

Bogdan Tarasiuk received his M.Sc. and Ph.D. in the Mathematics-Physics-Chemistry Faculty of Maria Curie-Skłodowska University in 1972 and 1984, respectively.

Research areas: Organic chemistry – polymer chemistry, chemistry of compounds of potential biological activity; synthesis, structure and properties of polymers containing sulfur in the main chain, particularly of polythioesters and polysulfides; synthesis, structure and properties of new compounds of potential biological activity; synthesis, structure and properties of urethane-acrylates as well as UV cured compositions for optical fibre coatings. Results of the investigations from these various fields were presented in over 60 scientific national and foreign journals, 10 patents and 81 communications.