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Studies on syntheses and biological activities of novel 3,5-dimethylpyrazole compounds containing [monohalogeno-(methyl)phenoxy]acyl group

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The results of the study on the syntheses and properties of new 3,5-dimethylpyrazole derivatives of 2-[methyl-, aryl-, monochloro-(bromo)phenoxy]alkane acids are presented. The compounds were synthesised during the reaction of 2-(aryloxy)alkanoic chlorides with an on 3,5-dimethylpyrazole and diethylaniline. The chemical structure of the newly obtained derivatives was confirmed through elementary and spectrophotometer FTIR analysis and spectroscopy of ^{1}H-NMR. Their physico-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-(4-chloro-2-methylphenoxyacetyl)-3,5-dimethylpyrazole and 1-[2-(4-chloro-3,5-di-methylphenoxy)propio-nyl]-3,5-dimethylpyrazole.

Keywords: derivatives of the 3,5-dimethylpyrazole of the 2-[methyl-, aryl-, monochloro-(bromo)phenoxy]alkane acids; synthesis, structure, properties, herbicidal activity

1. INTRODUCTION

2-(Halogenophenoxy)alkylcarboxylic acids and their derivatives 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. We can consider (2,4-dichlorophenoxy)acetic acid as a derivative of 2,4-dichlorophenol into whose hydroxyl group an acetic acid residue has introduced [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-dichlorophenoxy)acetic 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 [3,5].

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 [4, 6-8].

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 [9-16]. Lately, it has concentrated on the research related to the synthesis of 3,5-dimethylpyrazole derivatives of the 2-[methyl-, aryl-, monochloro-, (monobromo)phenoxy]alkane acids.

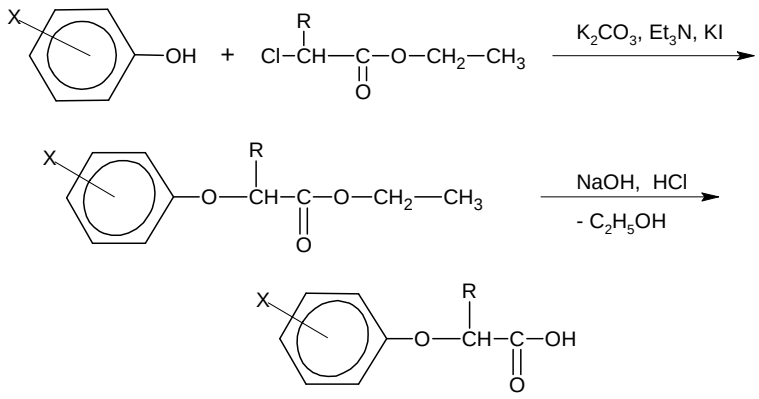
2. EXPERIMENTAL

Materials. 4-Methylphenol (mp = 32–34ºC), 4-phenylphenol (mp = 165–167ºC), 4-chlorophenol (mp = 43–45ºC), 4-bromophenol (mp = 64–68ºC), 4-chloro-2-methylphenol (mp = 45–48ºC), 4-chloro-3-methylphenol (mp = 65––68ºC), 2-bromo-4-methylphenol (bp = 213–214ºC), 4-chloro-3,5-dimethylphenol (mp = 114–116ºC), ethyl chloroacetate (bp = 143ºC), ethyl

2-chloropropionate (bp = 146–149ºC), thionyl chloride (bp = 79ºC) and 3,5-dimethylpyrazole (mp = 107–109ºC), all from Aldrich, Germany.

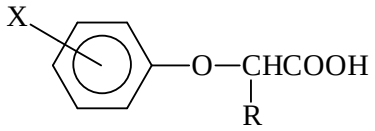
Synthesis of 2-aryloxyacetic (propionic) acids. At first, a convenient method was elaborated to synthesise the 2-(methyl-, phenyl-, monochloro-, monobromophenoxy)acetic (propionic) acids. Starting with suitable methyl-, phenyl-, chloro- or bromophenols and ethyl chloroacetate or ethyl 2-chloropropionate in presence of potassium carbonate, tributylamine and potassium iodide and cyclohexanone as solvent, at the temperature of 85ºC during 10 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.

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



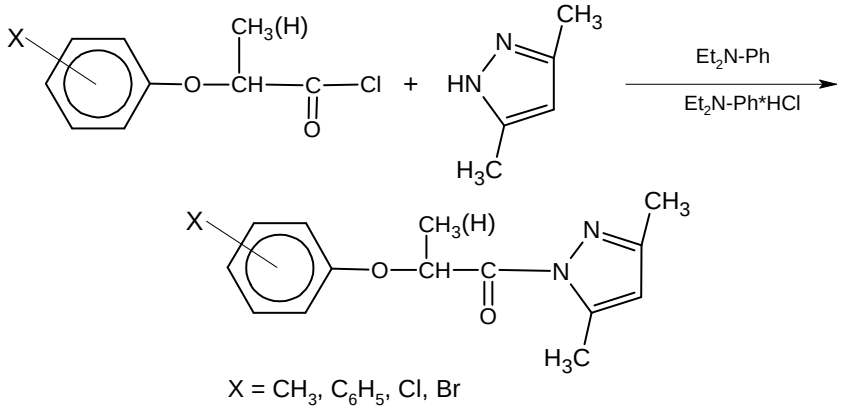
X = CH_3, C_6H_5, Cl or Br R = CH_3 or H

Tab. 1. Melting point of the 2-(aryloxy)acetic (propionic) acids



No.	Substituent		Melting point [°C]	Melting point [°C] acc. to literature
	R	X		
1	H	4-CH_3	141-142	140-142 /1/
2	CH_3	4-CH_3	101-102	101-102 /1/
3	H	4-C_6H_5	190-191	190-191 /1/
4	CH_3	4-C_6H_5	160-161	158-159 /3/
5	H	4-Cl	158-160	157-158 /1/
6	CH_3	4-Cl	115-116	114-115 /6/
7	H	4-Br	153.5-155	154 /2/
8	CH_3	4-Br	114-116	114.5-115.2 /5/
9	H	4-Cl, 2-CH_3	120-121	119-120 /1/
10	CH_3	4-Cl, 2-CH_3	96-96.5	92-93 /1/
11	H	4-Cl, 3-CH_3	178-179	177-178 /1/
12	CH_3	4-Cl, 3-CH_3	90-91	90-91 /1/
13	H	2-Br, 4-CH_3	144-145	144-145 /17/
14	CH_3	2-Cl, 5-CH_3	120-122	120-121 /18/
15	H	4-Cl, 3,5-$(CH_3)_2$	149-151	151 /1/
16	CH_3	4-Cl 3,5-$(CH_3)_2$	137-138	137-138 /1/

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:



Synthesis of 1-[2-(aryloxy)acyl]-3,5-dimethylpyrazole

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-dimethylpyrazole, 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 12–16ºC. 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 25ºC). In order to confirm the structure of the studied compounds, an elementary analysis was carried out as well as the spectrophotometer IR analysis (apparatus: spectrophotometer Perkin Elmer model 1725X; KBr) and spectroscopy of ^{1}H-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 [19].

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 investigated 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 was 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.

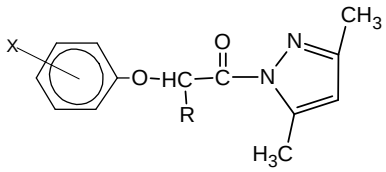
3. RESULTS AND DISCUSSION

New organic compounds were received, of the type 3,5-dimethylpyrazole derivative of 2-(methyl-, aryl-, monochloro- bromophenoxy)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.

The structure of the synthesised molecules of 1-[2-(aryloxy)acyl)-3,5-dimethylpyrazole confirms a very good agreement of the results of elementary analysis and the calculated contents of the atoms of C, H, N and the presence of the characteristic peaks of the absorption bands in the spectres in infrared FT--IR and the values of the magnetic proton resonance ^{1}H-NMR (Tables 4, 5 and 6).

The discussed organic compounds are colourless substances of melting temperature 87–147ºC. In the volume of 100 cm^3 of solvent at temperature 25ºC they dissolve in 1.5–7.1 g in ethanol, 8.0–28.0 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 240–320 g/mole) characterise with a considerable solubility in acetone and ethanol.

Tab. 2. Structure of the 1-[2-(aryloxy)acyl]-3,5-dimethylpyrazole



No of compound	Substituent		Molecular formula	Molecular weight
	R	X		
1	H	4-CH_3	$C_{14}H_{16}N_2O_2$	244.30
2	CH_3	4-CH_3	$C_{15}H_{18}N_2O_2$	258.32
3	H	4-C_6H_5	$C_{19}H_{18}N_2O_2$	306.37
4	CH_3	4-C_6H_5	$C_{20}H_{20}N_2O_2$	320.40
5	H	4-Cl	$C_{13}H_{13}ClN_2O_2$	264.71
6	CH_3	4-Cl	$C_{14}H_{15}ClN_2O_2$	278.74
7	H	4-Br	$C_{13}H_{13}BrN_2O_2$	309.16
8	CH_3	4-Br	$C_{14}H_{15}BrN_2O_3$	323.19
9	H	4-Cl, 2-CH_3	$C_{14}H_{15}ClN_2O_2$	278.74
10	CH_3	4-Cl, 2-CH_3	$C_{15}H_{17}ClN_2O_2$	292.77
11	H	4-Cl, 3-CH_3	$C_{14}H_{15}ClN_2O_2$	278.74
12	CH_3	4-Cl, 3-CH_3	$C_{15}H_{17}ClN_2O_2$	292.77
13	H	2-Br, 4-CH_3	$C_{14}H_{15}BrN_2O_2$	323.20
14	CH_3	2-Cl, 5-CH_3	$C_{15}H_{17}ClN_2O_2$	292.77
15	H	4-Cl, 3,5-$(CH_3)_2$	$C_{15}H_{17}ClN_2O_2$	292.77
16	CH_3	4-Cl, 3,5-$(CH_3)_2$	$C_{16}H_{19}ClN_2O_2$	306.80

Tab. 3. Yield of reaction, melting point and solubility of the 1-[2-(aryloxy)acyl]-3,5-dimethylpyrazole

No of comp.	Yield [wt. %]	Melting point [°C]	Solubility [g/100 cm^3]		
			Acetone	Ethanol	Water
1	80	109-111	24	4,5	0.1
2	81	87-89	28	6,5	0.2
3	71	145-147	8	1,5	-
4	69	129-131	11	2,0	-
5	69	141-142	18	3,9	-
6	65	87-88	21	5,0	-
7	81	139-141	13	5,1	-
8	83	101-102	15	5,5	-
9	78	119-120	20	4,3	0.05
10	74	90-91	25	7,1	0.1
11	83	130-131	15	3,1	-
12	70	101-102	19	4,2	-
13	79	135-137	11	2,5	-
14	78	98-100	15	3,7	-
15	80	136-137	9	2,9	-
16	78	120-122	12	3,4	-

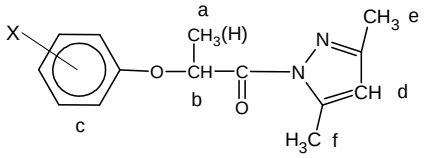
Tab. 4. The results of elemental analyses of the 1-[2-(aryloxy)acyl]-3,5--dimethylpyrazole

No of compound	Calculated [wt.%]			Found [wt.%]		
	C	H	N	C	H	N
1	68.83	6.60	11.47	68.85	6.45	11.51
2	69.75	7.02	10.84	69.50	7.13	10.67
3	74.49	5.92	9.14	74.95	6.07	9.12
4	74.97	6.29	8.74	74.71	6.49	8.85
5	58.99	4.95	10.58	58.79	5.09	10.81
6	60.32	5.24	10.05	60.52	5.45	10.50
7	50.51	4.24	9.06	50.31	4.41	9.13
8	52.03	4.68	8.67	52.31	4.82	8.70
9	60.32	5.42	10.05	60.29	5.25	10.15
10	61.54	5.85	9.57	61.73	5.65	9.71
11	60.32	5.42	10.05	60.55	5.49	10.01
12	61.54	5.85	9.57	61.57	5.95	9.79
13	52.03	4.68	8.67	52.09	4.83	8.75
14	61.54	5.85	9.57	61.49	5.79	9.87
15	61.54	5.85	9.57	61.41	5.59	9.77
16	62.64	6.24	9.13	62.73	6.31	9.03

Tab. 5. The results of FT-IR analysis of 1-[2-(aryloxy)acyl]-3,5-dimethylpyrazole

No	C-H $_{Ar}$	CH_3,CH_2,CH	C=O	Ph -O- CH	C=C_{Ar}
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, 3021	2987, 2967, 2920	1735	1251, 1045	1650, 1586, 1486
8	3075, 3021	2986, 2965, 2926	1734	1250, 1045	1650, 1585, 1486
9	3075, 3020	2987, 2965, 2920	1734	1252, 1043	1650, 1585, 1484
10	3075, 3018	2988, 2966, 2927	1734	1250, 1048	1650, 1586, 1487
11	3075, 3018	2986, 2967, 2927	1734	1250, 1043	1650, 1586, 1487
12	3075, 3018	2987, 2964, 2926	1735	1250, 1043	1650, 1586, 1487
13	3075, 3018	2984, 2966, 2925	1736	1250, 1044	1650, 1586, 1487
14	3075, 3018	2988, 2965, 2928	1734	1250, 1046	1650, 1586, 1487
15	3075, 3018	2986, 2965, 2926	1734	1250, 1046	1650, 1585, 1487
16	3075, 3018	2987, 2965, 2927	1734	1250, 1046	1650, 1585, 1487

Tab. 6. Spectroscopy of ^{1}H-NMR of the 1-[2-(aryloxy)acyl]-3,5-dimethylpyrazole



No of comp.	C<u>H</u>$_3$-CH-O a	C<u>H</u>$_3$-Ph X	N=C-C<u>H</u>$_3$ e C=C-C<u>H</u>$_3$ f	O-C<u>H</u>$_2$- b	O-C<u>H</u>-CH_3 b C=C-<u>H</u> d	Ph- <u>H</u> c
1	-	s; 2.2 3xH	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; 2.1; 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; 2.1; 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; 2.1; 3xH s; 2.5; 3xH	-	m; 5.9-6.1; 2xH	m; 7.2-7.6 4xH
9	-	s; 2.2 3xH	s; 2.2; 3xH s; 2.6; 3xH	s; 5.9 2xH	s; 6.1; 1xH	m; 7.2-7.6 3xH

10	d;1.8; 3xH J=6.8 Hz	s; 2.2 3xH	s; 2.1; 3xH s; 2.5; 3xH	-	m; 5.9-6.1; 2xH	m; 7.2-7.6 3xH
11	-	s; 2.2 3xH	s; 2.2; 3xH s; 2.6; 3xH	s; 5.9 2xH	s; 6.1; 1xH	m; 7.2-7.6 3xH
12	d;1.7; 3xH J=6.6 Hz	s; 2.2 3xH	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; 2.2; 3xH s; 2.6; 3xH	s; 5.9 2xH	s; 6.1; 1xH	m; 7.2-7.6 3xH
14	d;1.8; 3xH J=6.6 Hz	s; 2.2 3xH	s; 2.2; 3xH s; 2.6; 3xH	-	m; 5.9-6.1; 2xH	m; 7.2 -7.6 3xH
15	-	s; 2.2 6xH	s; 2.2; 3xH s; 2.5; 3xH	s; 5.9 2xH	s; 6.1; 1xH	s; 7.5 2xH
16	d;1.8; 3xH J=6.6 Hz	s; 2.2 6xH	s; 2.2; 3xH s; 2.6; 3xH	-	m; 5.9-6.1; 2xH	s; 7.5 2xH

Biological screening results. The 3,5-dimethylpyrazole 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 bioidicators. The primary data are presented in Table 7 and Figures 1, 2.

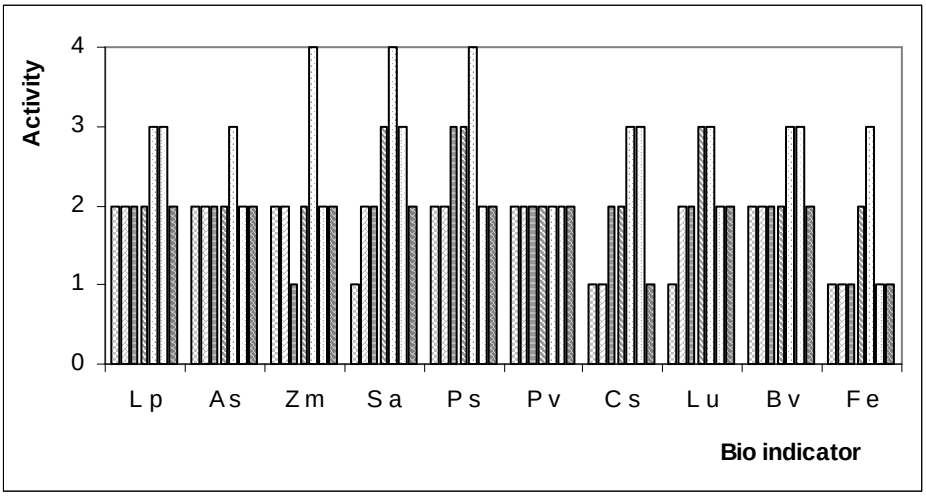


Fig. 1. Phytocidal activity of the 1-[2-aryloxyacetyl(propionyl)]-3,5-dimethylpyrazole No 3, 4, 5, 9, 10, 14 and 16 in preemergence application

Tab. 7. Phytocidal activity of the 1-[2-(halogenoaryloxy)acetyl(propionyl)]-3,5--dimethylpyrazole in of screening test

	Compound no						
Bioindicator	3	4	5	9	10	14	16
Lolium perenne L	2* 1**	2 1	2 0	2 1	3 1	3 1	2 0
Avena sativa L	2 1	2 1	2 0	2 1	3 2	2 1	2 0
Zea mays L	2 1	2 1	1 1	2 2	4 1	2 2	2 1
Sinapis alba L	1 0	2 1	2 2	3 3	4 3	3 3	2 1
Pisum sativum L	2 2	2 1	3 1	3 2	4 3	2 2	2 2
Phaseolus vulgaris L	2 1	2 0	2 1	2 2	2 3	2 2	2 2
Cucumis sativus L	1 1	1 0	2 2	2 1	3 2	3 2	1 2
Linum usitatissimum L	1 0	2 0	2 1	3 2	3 3	2 1	2 1
Beta vulgaris L	2 1	2 1	2 0	2 1	3 1	3 2	2 1
Fagopyrum esculentum Moench	1 1	1 0	1 0	2 0	3 1	1 0	1 1

Application: (*) preemergence, (**) postemergence.
Phytotoxicity: rating scale ranged from 0 to 4
(0 – no injury, 4 – complete death plant) [19].

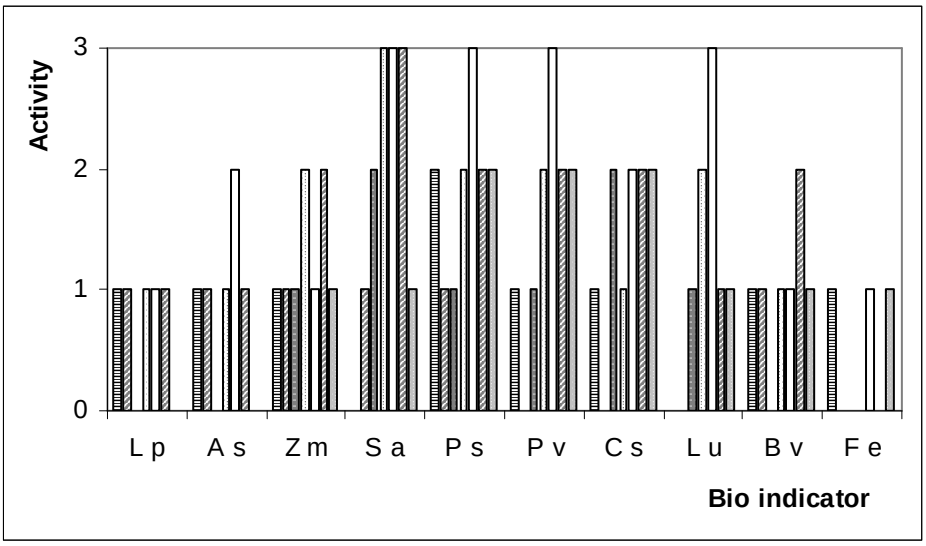


Fig. 2. Phytocidal activity of the 1-[2-aryloxyacetyl(propionyl)]-3,5-dimethylpyrazole No 3, 4, 5, 9, 10, 14 and 16 in postemergence application

The highest phytocidal activity was lagerly confined to the compounds No. 3, 4, 5, 9, 10, 14 and 16. 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- and post- emergence applications. The best compounds: 1-[2-(4-chloro-2-methylphenoxy)propionyl]--3,5-dimethylpyrazole (derivative No. 10) good controlled *dicotyledonous* weed species at the dose 2.5 and 1.25 kg a.i. per ha.

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-(4-chloro-2-methylphenoxy)propionyl]-3,5--dimethylpyra-zole, 2-(4-chloro-2-methylphenoxy)propane acid and 3,5--dimethylpyrazole 2-(4-chloro-2-methylphenoxy)propionate. The most active compound against *dicotyledons* weed species being the 3,5-dimethylpyrazole derivative of 2-(chlorophenoxy)propionic acid, next the salt and free acid, but 3,5-dimethylpyrazole showed no herbicidal activity.

In summary, the 3,5-dimethylpyrazole derivatives of 2-(halogen--phenoxy)alkane acids showed good herbicidal activity at pre- and post--emergence application.

4. REFERENCES

[1] M. E. Synerholm and P. W. Zimmerman, *Contrib. Boyce Thompson Inst*., **14** (1945) 91-103.
[2] L. Haslelberg, *J. Org. Chem.* **12** (1947) 426.
[3] H. R. Lewis, J. R. Housley, H. C. Richards, J. S. Nicholson, M. W. Bakes, S. S. Adams, *Pat. Brit*., 916,242 (1963), C.A. **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** (1962) 501-504.
[6] D. G. Crosby, *Advances in Pesticide Science*, H. Geisbuhler (ed). Oxford: Pergamon Press, 1979,V 3, p.569.
[7] J. B. Pillmoor et al., *Progress in Pesticide Biochemistry*, D.H. Hutson and T.R. Roberts (ed). Wiley, Chichester 1981, p.147.
[8] N. N. Melnikow, *Pestitside*, K.W. Nowozyw (ed). Khimiya., Moscow, 1987, p.226.
[9] W. Podkościelny, B. Tarasiuk, Z. Zimińska, *Przem. Chem.*, **73 (**1994) 466-468.
[10] E. Bakuniak et al., *Pestycydy*, **1** (1993) 21-27.
[11] B. Tarasiuk, *Pestycydy*, **1** (1996) 5-13.
[12] B. Tarasiuk, W. Podkościelny, *Przem. Chem.*, **74** (1995) 250-251.
[13] B. Tarasiuk, W. Podkościelny, Z. Zimińska, M. Krawczyk, *Pestycydy*, **1** (2000) 5.
[14] B. Tarasiuk, W. Podkościelny, *Annales UMCS, Sectio AA*, **LVI, 19** (2000) 282.
[15] B. Tarasiuk, *Annals of the Polish Chemical Society*, **2001** 46.
[16] W. W. Sułkowski (ed). Copyright: The Polish Chemical Society, Katowice, 2001.
[17] B. Tarasiuk, *Annals of the Polish Chemical Society*, **2003** 46, J. Narkiewicz-Michałek, W. Rudziński (ed). Copyright: The Polish Chemical Society, Lublin, 2003.
[18] A. Tako, K. Ongania, K. Wurst, *Monatsh. Chem.* **128(11)** (1997) 1149.
[19] A. Fredga et al., *Ark. Kemi.* **32** (1970/1974) 301.
[20] E. Bakuniak et al., *Pestycydy*, **4** (1978) 12.

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