

## Syntheses, structures and properties of halogenoanilides derivatives of dichlorophenoxyacetic acids

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The results of the study on the syntheses and properties of halogenoanilides derivatives of dichlorophenoxyacetic acids are presented. Compounds were synthesized during the reaction of dichlorophenoxyacetic chlorides with halogenoaniline and N,N-diethylaniline or dichlorophenoxyacetic acids with halogenoanilines and phosphorus oxychloride. The chemical derivatives were isolated with high yield and identified on the basis of elemental analysis, FTIR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy as well. Their physico-chemical properties were examined, along with their fungicidal, insecticidal, acaricidal and herbicidal activity. It was found that the highest herbicidal activity characterizes the derivatives of 2,4-dichlorophenoxyacet-4-fluoroanilide, 2,4-dichlorophenoxyacet-3-trifluoromethylanilide, 2,5-dichlorophenoxyacet-3-trifluoromethylanilide and 2,4-dichlorophenoxyacet-4-chloro-3-fluoroanilide.

### 1. INTRODUCTION

Derivatives of phenoxy acids show 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 [3].

The physiological activity of phenoxyacetic acid increases when a halogen such as fluorine or chlorine is introduced into the aromatic ring, 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 substituent 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 [1,3].

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 [1,3,4].

To reach the final scope it is necessary to use definitely smaller doses of esters than those of their salts or free acids. Actual task for the researchers who carry out the investigation of 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 of M. Curie-Skłodowska University investigation has been carried out for many years in order to look for some new organic compounds of potential biological activity [5-14]. Lately, it has been concentrated on the research related to the synthesis of chloro-fluoro-anilides derivatives of dichlorophenoxyacetic acids.

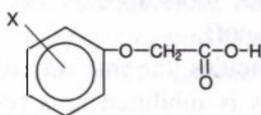
## 2. EXPERIMENTAL

**Materials.** 4-Fluoroaniline (bp = 187 °C/767mmHg) Aldrich, 4-chloro-3-trifluoromethylaniline (mp = 35–37 °C) Fluka Chemie AG; 4-fluoro-3-chloroaniline (mp = 41–44 °C) Merck, 3-trifluoromethylaniline (bp = 187 °C) Aldrich; 2,3-dichlorophenol (mp = 58–60°C), 2,4-dichlorophenol (mp = 42–43 °C), 2,5-dichlorophenol (mp = 56–58 °C), 2,6-dichlorophenol (mp = 65–68 °C), 3,4-dichlorophenol (mp = 66–68 °C), 3,5-dichlorophenol (mp = 67–68 °C), methyl bromoacetate (bp = 51–52 °C/15 mmHg), thionyl chloride (bp = 79 °C), phosphorus oxychloride (bp = 105 °C) all from Aldrich, Germany.

**Synthesis of dichlorophenoxyacetic acids.** At first, a convenient method was elaborated with the aim to synthesize the dichlorophenoxyacetic acids. Starting

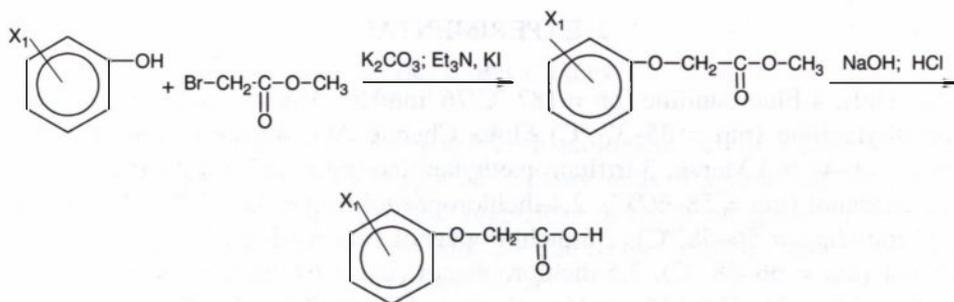
with suitable dichlorophenols and methyl bromoacetate in the presence of potassium carbonate, triethylamine and potassium iodide and N,N-dimethylformamide as solvent, at the temperature of 100 °C during 3 hours, methyl esters dichlorophenoxyacetic acids were prepared, isolated and purified. Then esters were hydrolysed for 2 hours in a water ethanol solution of sodium hydroxide at the temperature of 80 °C. 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. Structures and melting points of dichlorophenoxyacetic acids.



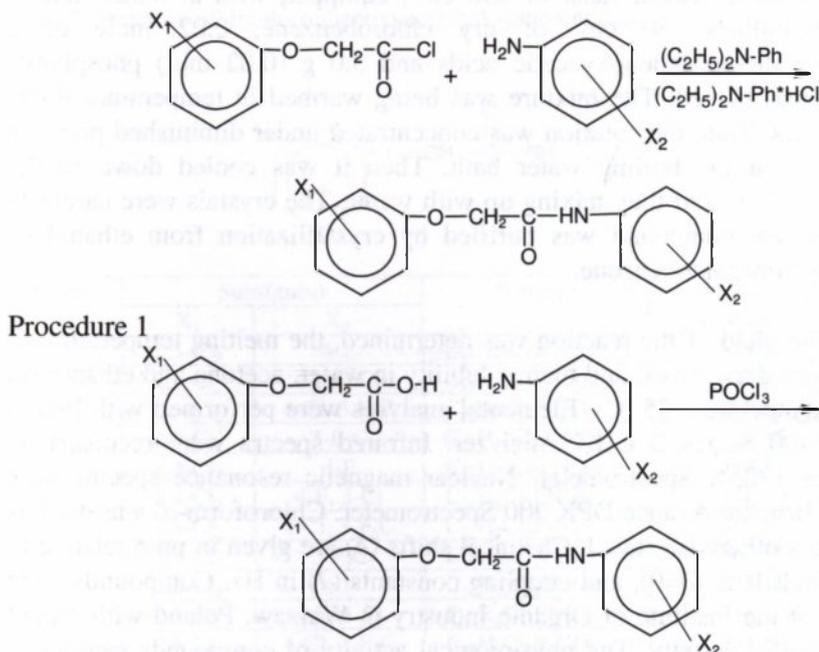
No.	Substituent X	Melting point [°C]	Melting point [°C] acc. to literature
1	2,3-Cl <sub>2</sub>	174–175	174–175 [16]
2	2,4-Cl <sub>2</sub>	140.5–141	141 [17]
3	2,5-Cl <sub>2</sub>	148–149	147–149 [18]
4	2,6-Cl <sub>2</sub>	134–135	134.5–135 [189]
5	3,4-Cl <sub>2</sub>	140–141	141 [18]
6	3,5-Cl <sub>2</sub>	117–118.5	117.5–118.5 [20]

The course of reaction that produced the dichlorophenoxyacetic acids was represented in the general scheme:



X<sub>1</sub> = 2,3-Cl<sub>2</sub>, 2,4-Cl<sub>2</sub>, 2,5-Cl<sub>2</sub>, 2,6-Cl<sub>2</sub>, 3,4-Cl<sub>2</sub>, 3,5-Cl<sub>2</sub>

The chlorides of dichlorophenoxyacetic acids were obtained by treating acids with thionyl chloride in excess. Dichlorophenoxyacet-chlorofluoroanilides were synthesized by the reaction of corresponding acid chlorides with an excess of chlorofluoroanilines and *N,N*-diethylaniline in benzene or corresponding dichlorophenoxyacetic acids with chloro-fluoro-anilines and phosphorus oxychloride in chlorobenzene. The course of reaction procedure 1 or 2 that produced the derivatives in question was represented in a general scheme:



Procedure 2

$X_1 = 2,3\text{-Cl}_2, 2,4\text{-Cl}_2, 2,5\text{-Cl}_2, 2,6\text{-Cl}_2, 3,4\text{-Cl}_2, 3,5\text{-Cl}_2$

$X_2 = 4\text{-F}; 4\text{-F}, 3\text{-Cl}; 4\text{-Cl}, 3\text{-F}_3\text{C}; 3\text{-F}_3\text{C}$

**Synthesis of the dichlorophenoxyacet-halogenoanilides. Procedure 1.** In a round bottom three-necked flask of 250 cm<sup>3</sup>, equipped with a mechanical stirrer, a thermometer, 0.025 mol of halogenoaniline, 50 cm<sup>3</sup> of dry benzene and 6.7 g (0.045 mol) *N,N*-diethylaniline were placed. While stirring the contents of the flask, a solution of 0.02 mole of a corresponding dichlorophenoxyacetic chlorides in 100 cm<sup>3</sup> of dry benzene was dropped into it, keeping the temperature within the range of 12–16 °C. 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 the temperature of 30–35 °C. 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. After it was cooled down to the temperature of 5°C, the crystals were carefully filtered. The raw compound was purified by crystallization from ethanol or mixture of cyclohexane-benzene.

**Synthesis of the dichlorophenoxyacet-halogenoanilides. Procedure 2.** In a round bottom three-necked flask of 250 cm<sup>3</sup>, equipped with a, 0.025 mol of chloro-fluoro-anilines, 50 cm<sup>3</sup> of dry chlorobenzene, 0.02 mole of a corresponding dichlorophenoxyacetic acids and 3.0 g (0.02 mol) phosphorus oxychloride was placed. The mixture was being warmed in temperature 90 °C through 2 hours. Then the solution was concentrated under diminished pressure while heating on the boiling water bath. Then it was cooled down to the temperature of 5 °C and they mixing up with water. The crystals were carefully filtered. The raw compound was purified by crystallization from ethanol or mixture of cyclohexane-benzene.

**Analyses.** 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<sup>3</sup> of temperature 25 °C). Elemental analyses were performed with Perkin Elmer PE 2400 Series II CHN Analyzer. Infrared spectra were recorded on Perkin Elmer 1725X Spectrometer. Nuclear magnetic resonance spectra were recorded on Bruker Avance DPX 300 Spectrometer. Chloroform-*d*<sub>1</sub> was used as solvent, unless otherwise stated. Chemical shifts ( $\delta$ ) are given in ppm relative to the tetramethylsilane ( $\delta=0$ ), and coupling constants (*J*) in Hz. Compounds were investigated at the Institute of Organic Industry in Warsaw, Poland with regard to their biological activity. The physiological activity of compounds mentioned above was studied against some insects, plants and fungi [12].

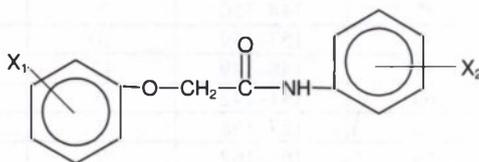
The studies of insecticidal activity were carried out in the laboratory, using some bioindicators, such as *Musca domestica* and *Tetranychus urticae* Koch. In the investigations, a sample of 0.1% acetone solution of the investigated compounds in the case of *Tetranychus urticae* Koch, and 25  $\mu$ g of *Musca domestica* after 48 hours used the mortality test of the bioindicators had been carried out. The fungicidal activity was studied *in vitro*, using the fungi: *Alternaria 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 chloro-fluoro-anilides derivatives of dichlorophenoxyacetic acids were prepared in two ways. These derivatives were getting with the high yield.

The data concerning the structure of these compounds, the yield of reaction, melting points and their solubility in three basic solvents are gathered in Tables 2 and 3.

Tab. 2. Structure of dichlorophenoxyacet-halogenoanilides.



Comp. no.	Substituent		Formula	Molecular mass
	X <sub>1</sub>	X <sub>2</sub>		
1	2,3-Cl <sub>2</sub>	4-F	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> FNO <sub>2</sub>	314.15
2	2,3-Cl <sub>2</sub>	4-F, 3-Cl	C <sub>14</sub> H <sub>9</sub> Cl <sub>3</sub> FNO <sub>2</sub>	348.59
3	2,3-Cl <sub>2</sub>	4-Cl, 3-F <sub>3</sub> C	C <sub>15</sub> H <sub>9</sub> Cl <sub>3</sub> F <sub>3</sub> NO <sub>2</sub>	398.60
4	2,3-Cl <sub>2</sub>	3-F <sub>3</sub> C	C <sub>15</sub> H <sub>10</sub> Cl <sub>2</sub> F <sub>3</sub> NO <sub>2</sub>	364.15
5	2,4-Cl <sub>2</sub>	4-F	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> FNO <sub>2</sub>	314.15
6	2,4-Cl <sub>2</sub>	4-F, 3-Cl	C <sub>14</sub> H <sub>9</sub> Cl <sub>3</sub> FNO <sub>2</sub>	348.59
7	2,4-Cl <sub>2</sub>	4-Cl, 3-F <sub>3</sub> C	C <sub>15</sub> H <sub>9</sub> Cl <sub>3</sub> F <sub>3</sub> NO <sub>2</sub>	398.60
8	2,4-Cl <sub>2</sub>	3-F <sub>3</sub> C	C <sub>15</sub> H <sub>10</sub> Cl <sub>2</sub> F <sub>3</sub> NO <sub>2</sub>	364.15
9	2,5-Cl <sub>2</sub>	4-F	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> FNO <sub>2</sub>	314.15
10	2,5-Cl <sub>2</sub>	4-F, 3-Cl	C <sub>14</sub> H <sub>9</sub> Cl <sub>3</sub> FNO <sub>2</sub>	348.59
11	2,5-Cl <sub>2</sub>	4-Cl, 3-F <sub>3</sub> C	C <sub>15</sub> H <sub>9</sub> Cl <sub>3</sub> F <sub>3</sub> NO <sub>2</sub>	398.60
12	2,5-Cl <sub>2</sub>	3-F <sub>3</sub> C	C <sub>15</sub> H <sub>10</sub> Cl <sub>2</sub> F <sub>3</sub> NO <sub>2</sub>	364.15
13	2,6-Cl <sub>2</sub>	4-F	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> FNO <sub>2</sub>	314.15
14	2,6-Cl <sub>2</sub>	4-F, 3-Cl	C <sub>14</sub> H <sub>9</sub> Cl <sub>3</sub> FNO <sub>2</sub>	348.59
15	2,6-Cl <sub>2</sub>	4-Cl, 3-F <sub>3</sub> C	C <sub>15</sub> H <sub>9</sub> Cl <sub>3</sub> F <sub>3</sub> NO <sub>2</sub>	398.60
16	2,6-Cl <sub>2</sub>	3-F <sub>3</sub> C	C <sub>15</sub> H <sub>10</sub> Cl <sub>2</sub> F <sub>3</sub> NO <sub>2</sub>	364.15
17	3,4-Cl <sub>2</sub>	4-F	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> FNO <sub>2</sub>	314.15
18	3,4-Cl <sub>2</sub>	4-F, 3-Cl	C <sub>14</sub> H <sub>9</sub> Cl <sub>3</sub> FNO <sub>2</sub>	348.59
19	3,4-Cl <sub>2</sub>	4-Cl, 3-F <sub>3</sub> C	C <sub>15</sub> H <sub>9</sub> Cl <sub>3</sub> F <sub>3</sub> NO <sub>2</sub>	398.60
20	3,4-Cl <sub>2</sub>	3-F <sub>3</sub> C	C <sub>15</sub> H <sub>10</sub> Cl <sub>2</sub> F <sub>3</sub> NO <sub>2</sub>	364.15
21	3,5-Cl <sub>2</sub>	4-F	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> FNO <sub>2</sub>	314.15
22	3,5-Cl <sub>2</sub>	4-F, 3-Cl	C <sub>14</sub> H <sub>9</sub> Cl <sub>3</sub> FNO <sub>2</sub>	348.59
23	3,5-Cl <sub>2</sub>	4-Cl, 3-F <sub>3</sub> C	C <sub>15</sub> H <sub>9</sub> Cl <sub>3</sub> F <sub>3</sub> NO <sub>2</sub>	398.60
24	3,5-Cl <sub>2</sub>	3-F <sub>3</sub> C	C <sub>15</sub> H <sub>10</sub> Cl <sub>2</sub> F <sub>3</sub> NO <sub>2</sub>	364.15

Tab. 3. Yield of reaction, melting point and solubility of dichlorophenoxyacet-halogenoanilides

Comp. no.	Procedure no.	Yield [wt. %]	M. p. [°C]	Solubility [g/100 cm <sup>3</sup> ]		
				Acetone	Ethanol	Water
1	1	59	151–152	10	3.0	0.1
2	1	90	160–161	12	1.5	0.1
3	1	83	157–158	10	1.5	-
4	1	78	138–139	16	2.0	0.05
5	1	66	119–121	7	2.5	0.1
6	1	89	148–150	8	2.0	-
7	1	83	157–159	10	2.5	-
8	1	81	148–149	12	3.0	0.05
9	2	63	141–142	9	2.0	-
10	2	78	157–158	7	1.5	-
11	2	83	161–162	9	1.5	-
12	1	79	155–156	10	2.0	-
13	1	60	112–113	10	3.1	0.1
14	1	80	142–143	13	2.5	-
15	1	75	147–148	11	2.0	-
16	1	71	139–140	16	3.0	0.05
17	2	67	122–123	7	1.5	0.05
18	2	73	149–151	6	1.0	-
19	1	78	159–160	7	1.0	-
20	1	75	145–146	9	2.0	-
21	2	71	148–149	8	1.0	-
22	2	89	155–156	7	0.5	-
23	2	80	161–162	6	0.5	-
24	1	83	131–132	8	1.0	-

The structure of dichlorophenoxyacet-halogenoanilides was confirmed by a very good agreement between the theoretical and the calculated contents in the C, H, N atoms (Table 4) and the presence of characteristic peaks in the Fourier transform infrared spectra (Figure 1 and Table 5) and the nuclear magnetic resonance shift values (Tables 6–9).

Important absorption peaks observed in the dichlorophenoxyacet-halogenoanilides spectra include those corresponding to the carbonyl group at 1690–1702 cm<sup>-1</sup>, the H-C stretching vibration in amide group at 3385–3388 cm<sup>-1</sup>, the H-C stretching vibrations in phenyl ring at 3107–3041 cm<sup>-1</sup>, CH<sub>2</sub>, stretching vibrations at 2920–2987 cm<sup>-1</sup>, stretching vibrations of the C=C in aromatic ring at 1605–1444 cm<sup>-1</sup>, and stretching vibrations of the Ph-O-C<sub>sym., asym.</sub> at 1251 cm<sup>-1</sup> and 1075 cm<sup>-1</sup>.

In the <sup>1</sup>H NMR spectrum of dichlorophenoxyacet-halogenoanilides, all signals corresponding to the proposed structure were observed in chloroform-*d*<sub>1</sub>.

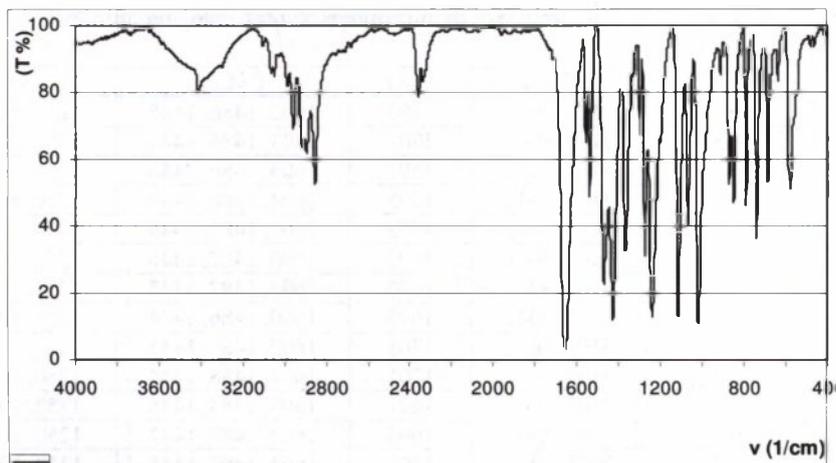


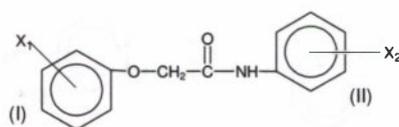
Fig. 1. FTIR spectra of 2,4-dichlorophenoxyacet-4-fluoroanilide.

Tab. 4. The results of elemental analysis of dichlorophenoxyacet-halogenoanilides.

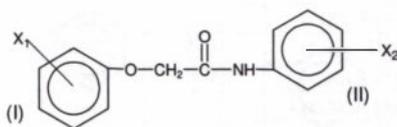
Comp. no.	Calculated [wt. %]			Found [wt. %]		
	C	H	N	C	H	N
1	53.53	3.21	4.46	53.43	3.44	4.40
2	48.24	2.60	4.02	48.45	2.67	4.09
3	45.20	2.28	3.51	45.25	2.20	3.50
4	49.48	2.77	3.85	49.56	2.71	3.88
5	53.53	3.21	4.46	53.60	3.27	4.40
6	48.24	2.60	4.02	48.19	2.65	4.00
7	45.20	2.28	3.51	45.39	2.29	3.52
8	49.48	2.77	3.85	49.55	2.74	3.80
9	53.53	3.21	4.46	53.38	3.26	4.41
10	48.24	2.60	4.02	48.19	2.63	4.00
11	45.20	2.28	3.51	45.01	2.26	3.55
12	49.48	2.77	3.85	49.59	2.72	3.90
13	53.53	3.21	4.46	53.60	3.29	4.60
14	48.24	2.60	4.02	48.40	2.62	4.20
15	45.20	2.28	3.51	45.29	2.26	3.48
16	49.48	2.77	3.85	49.35	2.79	3.81
17	53.53	3.21	4.46	53.29	3.22	4.41
18	48.24	2.60	4.02	48.13	2.61	4.18
19	45.20	2.28	3.51	45.18	2.22	3.59
20	49.48	2.77	3.85	49.41	2.71	3.82
21	53.53	3.21	4.46	53.69	3.29	4.44
22	48.24	2.60	4.02	48.19	2.62	4.21
23	45.20	2.28	3.51	45.30	2.20	3.56
24	49.48	2.77	3.85	49.40	2.79	3.87

Tab. 5. FTIR spectral data ( $\nu_{\max}/\text{cm}$ ) for dichlorophenoxyacet-halogenoanilides.

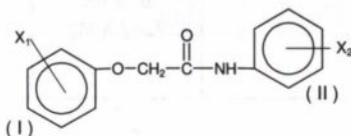
No	Ph-NH-CO	H-C=C <sub>ph</sub>	C=O	C=C <sub>ph</sub>	Ph -O- CH
1	3387	3105, 3042	1703	1602, 1486, 1445	1252, 1075
2	3385	3107, 3042	1701	1603, 1486, 1445	1251, 1075
3	3386	3107, 3041	1691	1605, 1486, 1446	1251, 1075
4	3388	3105, 3042	1695	1604, 1486, 1447	1250, 1075
5	3387	3105, 3042	1702	1601, 1485, 1445	1253, 1076
6	3385	3107, 3041	1697	1600, 1487, 1446	1252, 1074
7	3386	3107, 3041	1690	1603, 1487, 1447	1251, 1076
8	3388	3105, 3042	1697	1600, 1486, 1444	1251, 1075
9	3387	3105, 3042	1703	1602, 1486, 1445	1251, 1075
10	3385	3107, 3041	1701	1604, 1486, 1444	1250, 1075
11	3386	3107, 3043	1691	1605, 1484, 1445	1252, 1073
12	3388	3105, 3041	1695	1603, 1487, 1447	1250, 1078
13	3387	3105, 3042	1702	1604, 1487, 1445	1250, 1073
14	3385	3107, 3041	1697	1603, 1487, 1446	1250, 1073
15	3386	3107, 3043	1690	1606, 1487, 1444	1250, 1074
16	3388	3105, 3042	1697	1602, 1487, 1446	1250, 1076
17	3387	3105, 3041	1703	1603, 1487, 1445	1250, 1076
18	3385	3107, 3042	1701	1602, 1487, 1445	1252, 1073
19	3386	3107, 3041	1691	1604, 1487, 1446	1250, 1078
20	3388	3105, 3042	1695	1603, 1487, 1444	1250, 1073
21	3387	3105, 3042	1702	1605, 1487, 1445	1250, 1073
22	3385	3107, 3041	1697	1605, 1487, 1446	1250, 1074
23	3386	3107, 3043	1690	1604, 1487, 1445	1250, 1076
24	3388	3105, 3041	1697	1650, 1487, 1444	1250, 1076

Tab. 6.  $^1\text{H-NMR}$  spectral data ( $\sigma/\text{ppm}$ ) for phenyl rings (I) of dichlorophenoxyacet-halogenoanilides.

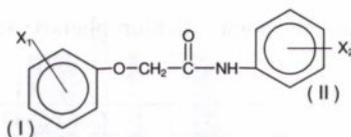
No.	X	H-C <sub>2</sub>	H-C <sub>3</sub>	H-C <sub>4</sub>	H-C <sub>5</sub>	H-C <sub>6</sub>
1	2,3-Cl <sub>2</sub>	-	-	d,d; 6.86 $J_o=8.8$ Hz; $J_m=2.5$ Hz	d; 7.08 $J_o=8.8$ Hz	d,d; 6.74 $J_o=8.8$ Hz; $J_m=2.5$ Hz
2	2,4-Cl <sub>2</sub>	-	d; 7.32 $J_m=2.5$ Hz	-	d,d; 7.17 $J_o=8.8$ Hz $J_m=2.5$ Hz	d; 6.94 $J_o=8.8$ Hz
3	2,5-Cl <sub>2</sub>	-	d; 7.41 $J_o=8.5$ Hz	d,d; 6.99 $J_o=8.5$ Hz $J_m=2.3$ Hz	-	d; 7.11 $J_m=2.3$ Hz
4	2,6-Cl <sub>2</sub>	-	d,d; 7.16 $J_o=8.8$ Hz; $J_m=2.5$ Hz	d; 6.78 $J_o=8.5$ Hz	d,d; 7.10 $J_o=8.8$ Hz; $J_m=2.5$ Hz	-
5	3,4-Cl <sub>2</sub>	d; 6.80 $J_m=2.8$ Hz	-	-	d; 7.14 $J_o=8.8$ Hz	d,d; 6.74 $J_o=8.8$ Hz $J_m=2.8$ Hz
6	3,5-Cl <sub>2</sub>	d; 6.82 $J_m=2.8$ Hz	-	d; 6.88 $J_m=2.8$ Hz	-	d; 6.82 $J_m=2.8$ Hz

Tab. 7.  $^1\text{H-NMR}$  spectral data ( $\sigma/\text{ppm}$ ) for phenyl rings (II) of dichlorophenoxyacet-halogenoanilides.

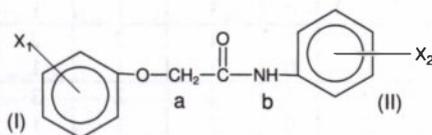
No.	$X_2$	H-C <sub>2</sub>	H-C <sub>3</sub>	H-C <sub>4</sub>	H-C <sub>5</sub>	H-C <sub>6</sub>
1	4-F	d,d; 7.36 $J_o=8.8$ Hz $J_m=2.5$ Hz	d; 6.89 $J_o=8.8$ Hz $J_m=2.5$ Hz	-	d,d; 6.89 $J_o=8.8$ Hz $J_m=2.5$ Hz	d,d; 7.36 $J_o=8.8$ Hz $J_m=2.5$ Hz
2	4-F, 3-Cl	d; 7.38 $J_m=2.5$ Hz	-	-	d; 6.83 $J_o=8.8$ Hz	d,d; 7.32 $J_o=8.8$ Hz; $J_m=2.5$ Hz
3	4-Cl, 3-F <sub>3</sub> C	d; 7.52 $J_o=8.8$ Hz	-	-	d; 7.41 $J_o=8.8$ Hz	d,d; 7.52 $J_o=8.8$ Hz; $J_m=2.5$ Hz
4	3-F <sub>3</sub> C	d; 8.16 $J_o=8.8$ Hz	-	d,d; 7.79 $J_o=8.5$ Hz $J_m=2.3$ Hz	d; 7.40 $J_o=8.5$ Hz	d,d; 7.60 $J_o=8.5$ Hz $J_m=2.3$ Hz

Tab. 8.  $^{13}\text{C}$  NMR spectral data ( $\sigma/\text{ppm}$ ) for phenyl rings no I of dichlorophenoxyacet-halogenoanilides.

No.	$X_1$	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>
1	2,3-Cl <sub>2</sub>	160.4	120.5	136.0	122.1	128.8	113.2
2	2,4-Cl <sub>2</sub>	157.2	124.3	130.3	127.1	127.9	115.3
3	2,5-Cl <sub>2</sub>	160.4	120.0	130.8	121.2	132.1	114.2
4	2,6-Cl <sub>2</sub>	159.5	121.5	127.9	123.0	127.9	121.3
5	3,4-Cl <sub>2</sub>	158.1	117.0	132.1	125.2	131.1	114.0
6	3,5-Cl <sub>2</sub>	161.3	117.0	132.8	125.1	131.0	114.5

Tab. 9.  $^{13}\text{C}$  NMR spectral data ( $\sigma/\text{ppm}$ ) for phenyl rings no II of dichlorophenoxyacet-halogenoanilides.

No.	X <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>
1	4-F	135.3	120.0	115.9	157.7	115.9	120.0
2	4-F, 3-Cl	136.6	120.3	122.1	138.1	117.1	118.1
3	4-Cl, 3-F <sub>3</sub> C	138.2	117.7	121.1	126.9	129.4	123.1
4	3-F <sub>3</sub> C	140.1	116.4	119.8	120.8	128.4	121.9



Assignments of the chemical shifts are as follows: (a) 5.8–5.9 ppm (singlet,  $\text{PhO}-\underline{\text{CH}}_2-\text{CO}$ ) and (b) 8.6–8.7 ppm (singlet, proton in NH amides). The signals corresponding to aromatic (I) and (II) protons could be observed at 6.80–8.16 ppm.

In the  $^{13}\text{C}$  NMR spectrum of dichlorophenoxyacet-halogenoanilides in chloroform- $d_1$  signals were observed at 68.2–68.5 and 165.9–169.1 ppm, which were assigned to methylene groups on  $\text{Ph}-\text{O}-\underline{\text{C}}\text{H}_2-\text{CO}$  carbon and the carbonyl carbon, respectively. The signals corresponding to phenyl carbons could be observed at 113.2–160.4 ppm.

The discussed organic compounds are colourless substances that dissolve in 0.5–3.1 g amount in  $100\text{ cm}^{-3}$  ethanol, 6.0–16.0 g in  $100\text{ cm}^{-3}$  acetone but in trace amounts in water, at  $25\text{ }^\circ\text{C}$  (Table 3). These compounds, while having a considerable large molecule, and so a large molecular weight (some 314–399 g/mole) characterised by a considerable solubility in acetone and ethanol.

**Biological screening results.** The chloro-fluoro-anilides derivatives of the dichlorophenoxyacetic 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 not sufficient for further interest, so they were eliminated from the test. The most interesting activity was noticed in phytocidal screen using ten plant bioindicators.

Results with regard to most active compounds were introduced in the Table 10 and Figures 2 and 3.

Tab. 10. Phytocidal activity of some dichlorophenoxyacet-halogenoanilides in the screening test.

Bioindicator	Compound no.							
	1	2	5	6	7	8	12	23
<i>Lolium perenne</i> – Lp	1* 0**	1 0	4 2	1 1	2 1	3 2	1 1	2 1
<i>Avena sativa</i> As	1 1	1 0	3 3	2 1	2 1	3 2	2 1	2 1
<i>Zea mays</i> Zm	1 1	1 0	3 3	1 1	2 1	3 1	1 1	2 1
<i>Sinapis alba</i> Sa	2 1	1 0	3 3	3 1	3 1	3 2	3 1	2 0
<i>Pisum sativum</i> Ps	1 0	1 0	4 3	2 1	2 1	3 2	2 1	2 1
<i>Phaseolus vulgaris</i> Phv	1 0	1 0	3 2	2 1	3 1	3 1	2 1	1 1
<i>Cucumis sativus</i> Cs	1 0	1 0	2 2	1 1	2 1	2 1	1 1	1 1
<i>Linum usitatissimum</i> Lu	1 1	0 0	3 1	1 1	1 2	2 2	1 1	1 1
<i>Beta vulgaris</i> Bv	1 1	0 0	3 2	1 1	2 2	2 1	1 1	2 1
<i>Fagopyrum esculentum</i> Fe	0 0	1 0	2 0	1 0	1 0	2 1	1 0	0 0

Application: ( \* ) preemergence, ( \*\* ) postemergence

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

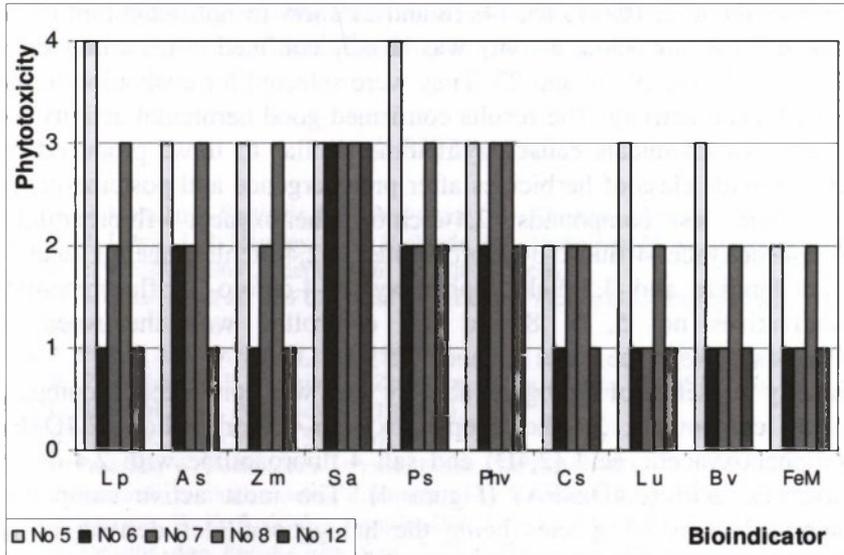


Fig. 2. Phytocidal activity of some the dichlorophenoxyacet-halogenoanilides in pre-emergence application.

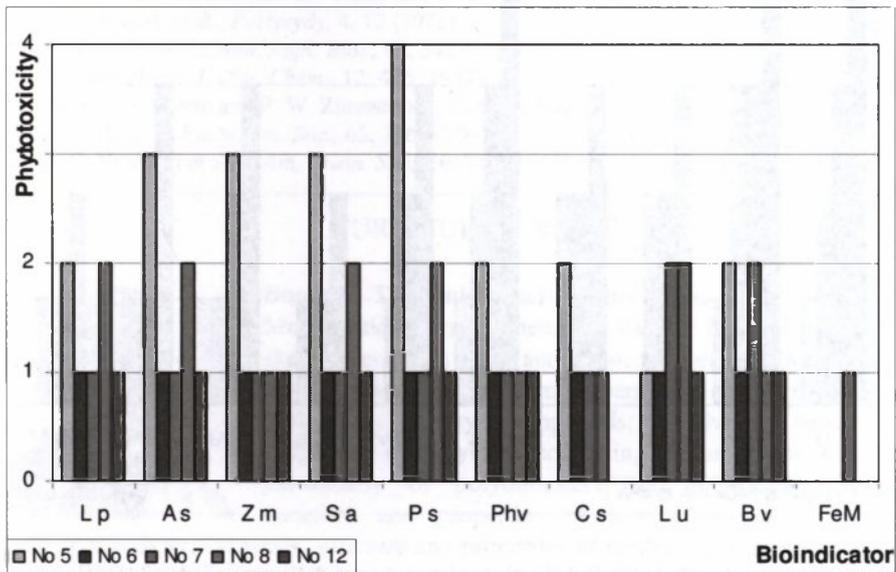


Fig. 3. Phytocidal activity of some the dichlorophenoxyacet-halogenoanilides in post-emergence application.

The compounds no 2, 10, 11, 13, 14, 18 and 21 show insignificant biological activity. The highest phytocidal activity was largely confined to the compounds no. 1, 5, 6, 7, 8, 12, 16, 19, 20 and 23. They were selected for evaluation in the 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 preemergence and postemergence applications. The best compounds: 2,4-dichloro-phenoxyacet-4-fluoroanilide, 2,4-dichlorophenoxyacet-4-fluoro-3-chloroanilide, 2,4-dichlorophenoxyacet-3-trifluoromethylanilide and 3,5-dichlorophenoxyacet-4-chloro-3-trifluoromethyl-anilide (derivatives no. 5, 6, 8 and 23) controlled well the weed of dicotyledonous species at the doses 2.5 and 1.25 kg a.i./ ha.

Additionally the series of biological activity tests was conducted to compare the following compounds: 2,4-dichlorophenoxyacet-4-fluoroanilide (2,4D4F), 2,4-dichlorophenoxyacetic acid (2,4D) and salt 4-fluoroaniline with 2,4-dichlorophenoxyacetic acid (2,4Dx4FA) (Figure 4). The most active compound against dicotyledons weed species being the halogenoanilides derivatives of dichlorophenoxyacetic acids, next the salts and free acids, but halogenoanilines showed no herbicidal activity.

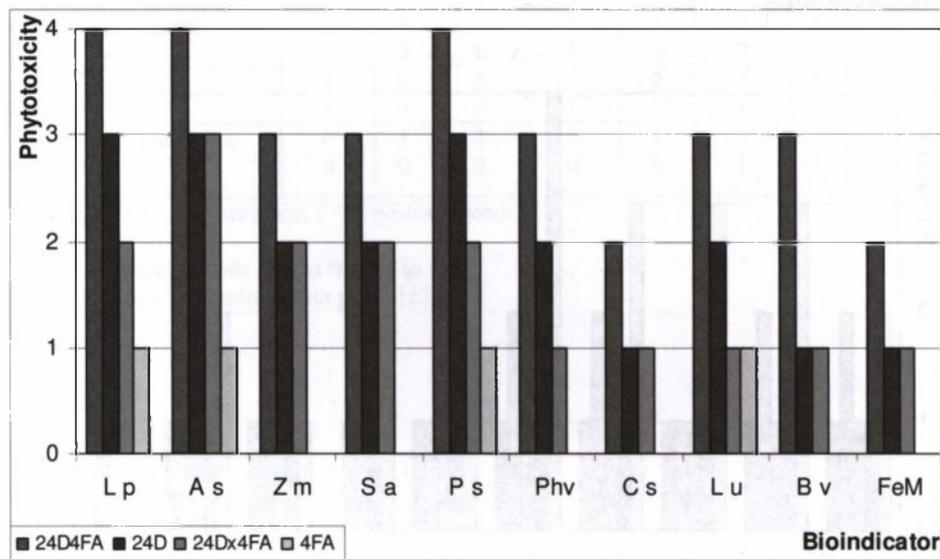


Fig. 4. Phytocidal activity of the 2,4-dichlorophenoxyacet-4-fluoroanilide (24D4FA), 2,4-dichlorophenoxyacetic acid (24D), salt 4-fluoroaniline and 2,4-dichlorophenoxyacetic acid (24Dx4FA), 4-fluoroaniline (4FA).

In summary, the chloro-fluoro-anilides derivatives of dichlorophenoxyacetic acids showed good herbicidal activity at preemergence and postemergence application.

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#### CURRICULUM VITAE



**Bogdan Tarasiuk** received his M.Sc. and Ph.D. in the Mathematics-Physics-Chemistry Faculty Maria Curie-Skłodowska University in 1972 and 1984, respectively. Research areas: organic chemistry - polymer chemistry, chemistry of potential biological activity compounds; 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 and urethane-epoxy-acrylates as well as UV cured compositions for optical fibers coatings. Results of the investigations from these various fields were presented in over 62 scientific national and foreign journals, 10 patents and 88 communications.