

Syntheses, structures and properties of halogenanilides derivatives of trichlorophenoxyacetic acids

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The results of the study on the syntheses and properties of halogenanilides derivatives of trichloro- phenoxyacetic acids are presented. Compounds were synthesized during the reaction of trichlorophenoxyacetic chlorides with halogenaniline and N,N-diethylaniline or trichlorophenoxyacetic acids with halogenanilines and phosphorus oxychloride. The chemical derivatives were isolated with high yield and identified on the basis of elemental analysis, FTIR, ¹H NMR and ¹³C 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 2,4,5-trichlorophenoxyacet-4-fluoroanilide, 2,4,5-trichlorophenoxyacet-4-chloro-3-(trifluoromethyl)anilide, 2,4,5-trichlorophenoxyacet-3-(trifluoromethyl)anilide and 2,4,5-trichlorophenoxyacet-4-chloro-3-fluoroanilide.

1. INTRODUCTION

Halogenphenoxyalkane acids and these derivatives show a high biological activity. Especially the ammonium and alkali metals salts of those acids were widely applied in many areas of agriculture, among the others as herbicides, fungicides and regulators of the plant growth [1-4]. The chemical properties of these herbicides are due to the aromatic radical (phenyl) and the presence of the carboxyl group. The physiological activity of halogenphenoxyalkane acids increases when a halogen such as fluorine, chlorine or bromine 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 phenolxyacetic acid, the activity of the compound grows insignificantly [3].

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].

These herbicides penetrate well into plants through their leaves and roots, but are used more frequently for spraying vegetating plants with aqueous solutions and emulsions. The spraying periods are established depending on the phase of stability of the cultivated plants, the sensitivity of the weeds, and the weather. When sprayed, the herbicides 2,4-dichlorophenoxyacetic acid and 4-chloro-2-methylphenoxyacetic acid get onto the leaves and stems in the form of minute drops, and to exhibit phytotoxic activity they must penetrate into the leaves, surmounting the barrier formed by the protective tissues. The herbicides may penetrate through the stomas, and also through the cuticle, which is permeable to hydrophilic and lipophilic compounds because it has micropores – ectoderm. Oil solutions of the herbicides penetrate better through the cuticle because they have a dissolving ability[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 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 halogenaryloxyalkane 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. C. Skłodowska University investigation has been carried out for many years in order to look for some new organic compounds of potential biological activity [5-12]. Lately, it has concentrated on the research related to the synthesis of chloro-, and (or) fluoro-anilides derivatives of 2,4,5- and 2,4,6-trichlorophenoxyacetic acids.

2. EXPERIMENTAL

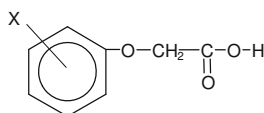
Materials.

4-Fluoroaniline (bp = 187°C/767mmHg), 4-chloro-3-trifluoromethylaniline (mp = 35-37°C), 4-fluoro-3-chloroaniline (mp = 41-44°C), 3-(trifluoromethyl)aniline (bp = 187°C), 4-chloroaniline (mp = 69-72°C), 3-chloro-4-methylaniline (mp = 24-25°C), 2,6-dichloroaniline (mp = 38-41°C), 3,4-dichloroaniline (mp = 69-71°C), 2,4,5-trichlorophenol (mp = 67-69°C), 2,4,6-trichlorophenol (mp = 64-66°C), methyl bromoacetate (bp = 51-52°C/15mmHg), thionyl chloride (bp = 79°C), phosphorus oxychloride (bp = 105°C) all from Aldrich, Germany.

Synthesis of 2,4,5- and 2,4,6-trichlorophenoxyacetic acids.

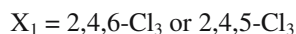
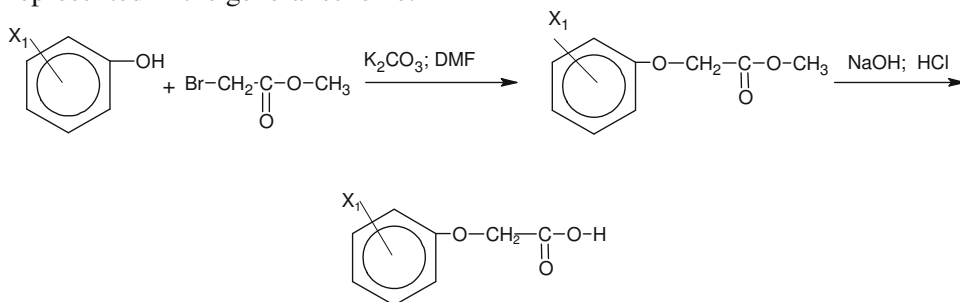
At first, a convenient method was elaborated with the aim to synthesize the trichlorophenoxyacetic acids. Starting with suitable 2,4,5- or 2,4,6-trichlorophenols and methyl bromoacetate in the presence of potassium carbonate, triethylamine and potassium iodide and N,N-dimethylformamide as solvent, at the temperature of 100°C during 6 hours, methyl esters trichlorophenoxyacetic acids were prepared, isolated and purified. Then esters were hydrolysed for 5 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 yield and melting points of 2,4,5- and 2,4,6-trichlorophenoxyacetic acids.

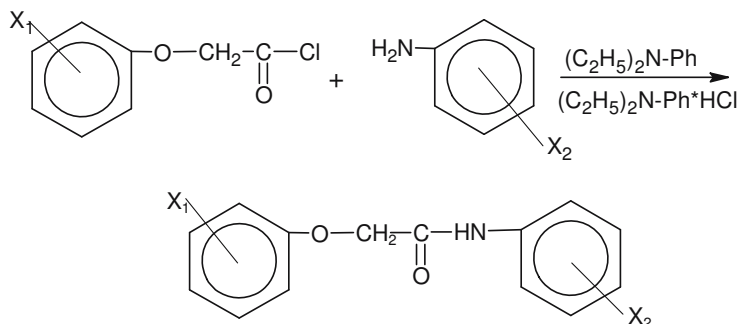


No.	Substituent	Yield [wt. %]	Melting point [°C]	Melting point [°C] acc. literature
	X			
1	2,4,5-Cl ₃	68	158-159	154-155 [1] 152-153 [15]
2	2,4,6-Cl ₃	65	179.7-181.5	177 [14] 190 [15] 179-181 [16]

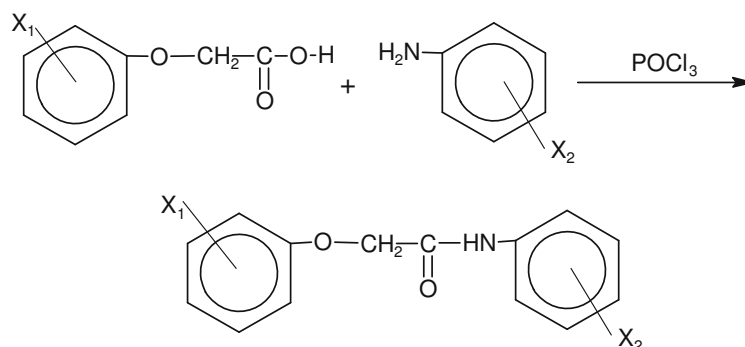
The course of reaction that produced the trichlorophenoxyacetic acids was represented in the general scheme:



The chlorides of trichlorophenoxyacetic acids were obtained by treating acids with thionyl chloride in excess. Trichlorophenoxyacet-chlorofluoroanilides were synthesized by the reaction of corresponding acid chlorides with an excess of chloro-fluoro-anilines and N,N-diethylaniline in benzene or corresponding trichlorophenoxyacetic 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 1



Procedure 2

$X_1 = 2,4,6\text{-Cl}_3$ or $2,4,5\text{-Cl}_3$

$X_2 = 4\text{-F}; 4\text{-F}, 3\text{-Cl}; 4\text{-Cl}, 3\text{-F}_3\text{C}; 3\text{-F}_3\text{C}; 4\text{-Cl}; 3\text{-Cl}, 4\text{-Me}; 2,6\text{-Cl}_2; 3,4\text{-Cl}_2$

Synthesis of the trichlorophenoxyacet-halogenanilides. Procedure 1.

In a round bottom three-necked flask of 250 cm³, equipped with a mechanical stirrer, a thermometer, 0.025 mol of halogenoaniline, 50 cm³ 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 moles of a corresponding trichlorophenoxyacetic chloride in 100 cm³ 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 N,N-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 30–35°C. The sediment of N,N-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 a of ethanol or mixture of cyclohexane – benzene.

Synthesis of the trichlorophenoxyacet-halogenanilides. Procedure 2.

In a round bottom three-necked flask of 250 cm³, equipped with a, 0.025 mol of chloro-fluoro-anilines, 50 cm³ of dry chlorobenzene, 0.02 mole of a corresponding trichlorophenoxyacetic acids and 3.0 g (0.02 mol) phosphorus oxychloride was placed.

The mixture was being warmed in temperature 110°C through 4 hours.

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

and they mixing up with water. The crystals were carefully filtered. The raw compound was purified by crystallization from a of ethanol or mixture of cyclohexane – benzene.

Analyses.

The yield of the reaction, the melting temperature of the synthesized derivatives, and their solubility in water, acetone and ethanol (in 100 cm³ of temperature 25°C) was determined.

Melting points were determined using a the Sanyo Gallenkamp Melting Point MPD 350 BM 3.5 Apparatus. 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*₁ was used as solvent, unless otherwise stated. Chemical shifts (δ) are given in ppm relative to the tetramethylsilane ($\delta=0$), and coupling constants (*J*) in Hz.

Obtained compounds were investigated with regard to their biological activity. The physiological activity of compounds mentioned above was studied against some insect, plants and fungi [13].

The studies of insecticidal activity were carried out in the laboratory, using some bioindicators, such as *Musca domestica* and *Tetranychus urticae* Koch. Investigated compounds were prepared in 0.1% acetone solution. This kind of solution acted on *Tetranychus urticae* Koch and *Musca domestica*. After 48 hours biological activity test of the bioindicators was made. The fungicidal activity was studied in vitro, using the fungi's: *Alternaria tenures*, *Botrytis cinerea*, *Rhizoctonia solani*, *Fusarium culmorum* or living plants covered with the spores of *Erysiphe graminis*. The phytocidal reaction of these compounds was studied before germination and after germination on 10 selected indicative plants. Investigated compounds in the quantity equal dose of 5 kg/hectare [13].

3. RESULTS AND DISCUSSION

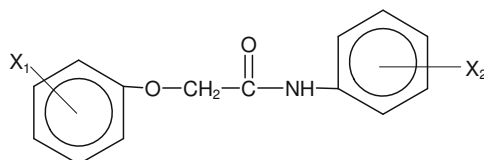
New chloro-, or (and) fluoro-anilides derivatives of 2,4,5- and 2,4,6-trichloro-phenoxyacetic acids were prepared with two ways. These derivatives were getting with the high yield.

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.

The structure of trichlorophenoxyacet-halogenanilides 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 of the absorption bands in the spectra's Fourier transform infrared spectrophotometer

(Figure 1 and Table 5) and the values of nuclear magnetic resonance spectrometer (Tables 6, 7).

Tab. 2. Structure of trichlorophenoxyacet-halogenanilides.



Comp. no.	Substituent		Formula	Molecular mass
	X ₁	X ₂		
1	2,4,5-Cl ₃	4-F	C ₁₄ H ₉ Cl ₃ FNO ₂	348.58
2	2,4,5-Cl ₃	4-F, 3-Cl	C ₁₄ H ₈ Cl ₄ FNO ₂	383.03
3	2,4,5-Cl ₃	4-Cl, 3-F ₃ C	C ₁₅ H ₈ Cl ₄ F ₃ NO ₂	433.04
4	2,4,5-Cl ₃	3-F ₃ C	C ₁₅ H ₉ Cl ₃ F ₃ NO ₂	398.59
5	2,4,5-Cl ₃	4-Cl	C ₁₄ H ₉ Cl ₄ NO ₂	365.04
6	2,4,5-Cl ₃	3-Cl,4-Me	C ₁₅ H ₁₁ Cl ₄ NO ₂	379.07
7	2,4,5-Cl ₃	2,6-Cl ₂	C ₁₄ H ₈ Cl ₅ NO ₂	399.48
8	2,4,5-Cl ₃	3,4-Cl ₂	C ₁₄ H ₈ Cl ₅ NO ₂	399.48
9	2,4,6-Cl ₃	4-F	C ₁₄ H ₉ Cl ₃ FNO ₂	348.58
10	2,4,6-Cl ₃	4-F, 3-Cl	C ₁₄ H ₈ Cl ₄ FNO ₂	383.03
11	2,4,6-Cl ₃	4-Cl, 3-F ₃ C	C ₁₅ H ₈ Cl ₄ F ₃ NO ₂	433.04
12	2,4,6-Cl ₃	3-F ₃ C	C ₁₅ H ₉ Cl ₃ F ₃ NO ₂	398.59
13	2,4,6-Cl ₃	4-Cl	C ₁₄ H ₉ Cl ₄ NO ₂	365.04
14	2,4,6-Cl ₃	3-Cl,4-Me	C ₁₅ H ₁₁ Cl ₄ NO ₂	379.07
15	2,4,6-Cl ₃	2,6-Cl ₂	C ₁₄ H ₈ Cl ₅ NO ₂	399.48
16	2,4,6-Cl ₃	3,4-Cl ₂	C ₁₄ H ₈ Cl ₅ NO ₂	399.48

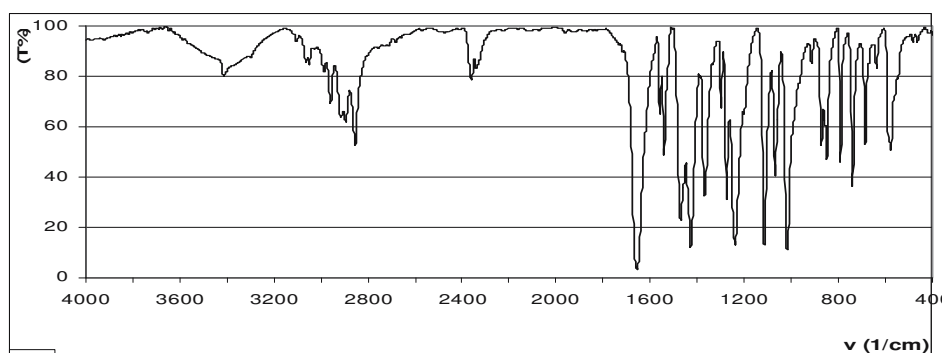


Fig. 1. FTIR spectra of 2,4,6-trichlorophenoxyacet-4-fluoroanilide.

Tab. 3. Yield of reaction, melting point and solubility of trichlorophenoxyacet-halogenanilides.

Comp. no.	Procedure No	Yield [wt. %]	M. p. [°C]	Solubility [g/100 cm ³]		
				Acetone	Ethanol	Water
1	2	72	180–181	8	3.0	–
2	2	81	210–212	10	1.0	0.05
3	1	88	155–156	8	1.0	0.1
4	1	83	192–194	12	2.0	0.05
5	2	69	198–199	5	2.0	–
6	1	89	149–150	7	2.0	–
7	2	82	198–200	8	2.0	–
8	2	85	219–220	6	2.5	–
9	2	73	197–198	9	2.5	–
10	2	85	228–230	11	1.5	0.05
11	1	89	168–170	9	1.5	0.05
12	1	87	197–199	13	2.0	0.10
13	2	68	203–205	6	1.5	–
14	1	88	169–171	8	2.0	–
15	2	75	219–221	9	2.0	–
16	2	77	227–228	8	1.5	–

Tab. 4. The results of elemental analysis of trichlorophenoxyacet-halogenanilides.

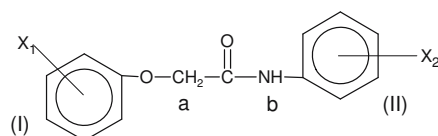
Comp. no.	Calculated [wt.%]			Found [wt.%]		
	C	H	N	C	H	N
1	48.24	2.60	4.02	48.40	2.58	4.01
2	43.90	2.11	4.96	43.99	2.10	4.98
3	41.60	1.86	3.23	41.70	1.89	3.35
4	45.20	2.28	3.51	45.15	2.21	3.50
5	46.06	2.49	3.84	46.27	2.50	3.82
6	47.53	2.92	3.70	47.55	2.93	3.75
7	42.09	2.02	3.51	42.13	2.09	3.55
8	42.09	2.02	3.51	42.28	2.01	3.47
9	48.24	2.60	4.02	48.19	2.65	4.06
10	43.90	2.11	4.96	43.87	2.13	4.89
11	41.60	1.86	3.23	41.57	1.90	3.29
12	45.20	2.28	3.51	45.33	2.31	3.59
13	46.06	2.49	3.84	46.13	2.54	3.90
14	47.53	2.92	3.70	47.59	2.87	3.62
15	42.09	2.02	3.51	42.01	2.01	3.49
16	42.09	2.02	3.51	42.23	2.10	3.50

Tab. 5. FTIR spectral data (ν_{\max}/cm) for trichlorophenoxyacet-halogenanilides.

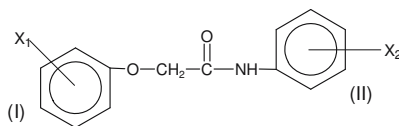
No	Ph-NH-CO	H-C=C _{Ph}	C=O	C=C _{Ph}	Ph-O-CH
1	3381	3105, 3042	1701	1602, 1486, 1445	1252, 1073
2	3382	3107, 3042	1701	1603, 1486, 1445	1251, 1074
3	3382	3107, 3041	1696	1605, 1486, 1446	1251, 1072
4	3381	3105, 3042	1695	1604, 1486, 1447	1250, 1071
5	3380	3105, 3042	1701	1601, 1485, 1445	1253, 1072
6	3382	3107, 3041	1697	1600, 1487, 1446	1252, 1071
7	3380	3107, 3041	1698	1603, 1487, 1447	1251, 1073
8	3381	3105, 3042	1697	1600, 1486, 1444	1251, 1071
9	3382	3105, 3042	1701	1602, 1486, 1445	1251, 1073
10	3383	3107, 3041	1701	1604, 1486, 1444	1250, 1074
11	3382	3107, 3043	1696	1605, 1484, 1445	1252, 1073
12	3381	3105, 3041	1697	1603, 1487, 1447	1250, 1071
13	3380	3105, 3042	1700	1604, 1487, 1445	1250, 1072
14	3382	3107, 3041	1697	1603, 1487, 1446	1250, 1073
15	3380	3107, 3043	1698	1606, 1487, 1444	1250, 1074
16	3381	3105, 3042	1697	1602, 1487, 1446	1250, 1072

Important absorption peaks observed in the trichlorophenoxyacet-halogenanilides spectra include those corresponding to the carbonyl group at $1690\text{--}1702\text{ cm}^{-1}$, the H-C stretching vibration in amide group at $3385\text{--}3388\text{ cm}^{-1}$, the H-C stretching vibrations in phenyl ring at $3107\text{--}3041\text{ cm}^{-1}$, CH₂, stretching vibrations at $2920\text{--}2987\text{ cm}^{-1}$, stretching vibrations of the C=C in aromatic ring at $1605\text{--}1444\text{ cm}^{-1}$, and stretching vibrations of the Ph-O-C_{sym., asym.} at 1251 cm^{-1} and 1075 cm^{-1} .

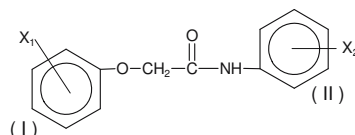
In the ¹H NMR spectrum of trichlorophenoxyacet-halogenanilides, all signal corresponding to the proposed structure were observed in chloroform-*d*₁.



Assignments of the chemical shifts are as follows: (a) $4.76\text{--}5.95\text{ ppm}$ (singlet, PhO-CH₂-CO) and (b) $8.67\text{--}8.70\text{ ppm}$ (singlet, proton in NH amides). The signals corresponding to aromatic (I) and (II) protons could be observed at $6.85\text{--}8.30\text{ ppm}$.

Tab. 6. $^1\text{H-NMR}$ spectral data (σ/ppm) for phenyl rings of trichlorophenoxyacet-halogenanilides.

No.	X ₁ or X ₂	<u>H-C</u> ₂	<u>H-C</u> ₃	<u>H-C</u> ₄	<u>H-C</u> ₅	<u>H-C</u> ₆
Phenyl ring (I)						
1	2,4,5-Cl ₃	-	d; 7.18 $J_p=0.6\text{Hz}$	-	-	d; 6.84 $J_p=0.6\text{Hz}$
2	2,4,6-Cl ₃	-	d; 7.42 $J_p=0.5\text{Hz}$	-	d; 7.42 $J_p=0.5\text{Hz}$	-
Phenyl ring (II)						
1	4-F	d,d; 7.60 $J_o=8.5\text{Hz}$ $J_m=2.0\text{Hz}$	d; 6.96 $J_o=8.5\text{Hz}$ $J_m=2.0\text{Hz}$	-	d,d; 6.96 $J_o=8.5\text{Hz}$ $J_m=2.0\text{Hz}$	d,d; 7.60 $J_o=8.5\text{Hz}$ $J_m=2.0\text{Hz}$
2	4-F, 3-Cl	d; 8.03 $J_m=2.0\text{Hz}$	-	-	d; 7.13 $J_o=8.5\text{Hz}$	d,d; 7.55 $J_o=8.5\text{Hz}$ $J_m=2.0\text{Hz}$
3	4-Cl, 3-F ₃ C	d; 8.12 $J_m=2.0\text{Hz}$	-	-	d; 7.40 $J_o=8.5\text{Hz}$	d,d; 7.72 $J_o=8.5\text{Hz}$ $J_m=2.0\text{Hz}$
4	3-F ₃ C	d; 8.06 $J_m=2.0\text{Hz}$	-	d,d; 7.19 $J_o=8.0\text{Hz}$ $J_m=2.0\text{Hz}$	d; 7.40 $J_o=8.0\text{Hz}$	d,d; 7.72 $J_o=8.0\text{Hz}$ $J_m=2.0\text{Hz}$
5	4-Cl	d,d; 7.57 $J_o=8.5\text{Hz}$ $J_m=2.0\text{Hz}$	d; 7.29 $J_o=8.5\text{Hz}$ $J_m=2.0\text{Hz}$	-	d,d; 7.29 $J_o=8.8\text{Hz}$ $J_m=2.5\text{Hz}$	d,d; 7.57 $J_o=8.5\text{Hz}$ $J_m=2.0\text{Hz}$
6	3-Cl,4-Me	d; 8.08 $J_m=2.0\text{Hz}$	-	-	d; 7.22 $J_o=8.5\text{Hz}$	d,d; 7.37 $J_o=8.5\text{Hz}$ $J_m=2.0\text{Hz}$
7	2,6-Cl ₂	-	d; 7.40 $J_o=8.0\text{Hz}$ $J_m=2.0\text{Hz}$	d; 7.24 $J_o=8.0\text{Hz}$	d; 7.40 $J_o=8.0\text{Hz}$ $J_m=2.0\text{Hz}$	-
8	3,4-Cl ₂	d; 8.30 $J_m=2.0\text{Hz}$	-	-	d; 7.36 $J_o=8.0\text{Hz}$	d,d; 7.52 $J_o=8.0\text{Hz}$ $J_m=2.0\text{Hz}$

Tab. 7. ^{13}C NMR spectral data (σ/ppm) for phenyl rings of trichlorophenoxyacet-halogenanilides.

No.	X ₁	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
Phenyl ring (I)							
1	2,4,5-Cl ₃	153.9	121.2	130.7	123.7	130.8	117.2
2	2,4,6-Cl ₃	150.9	129.5	129.5	129.1	129.5	129.5
Phenyl ring (II)							
1	4-F	135.1	122.6	116.9	156.8 163.3	116.9	122.6
2	4-F, 3-Cl	136.1	122.9	118.4	149.4 155.9	115.9	121.3
3	4-Cl, 3-F ₃ C	135.7	119.6	118.3	152.0 158.4	116.5	125.4
4	3-F ₃ C	139.2	118.2	128.1	119.5	129.8	123.1
5	4-Cl	137.1	121.0	129.4	122.7	129.4	121.0
6	3-Cl,4-Me	138.0	121.7	135.1	129.3	130.5	118.9
7	2,6-Cl ₂	134.2	136.5	127.8	128.3	127.8	136.9
8	3,4-Cl ₂	138.2	122.8	131.2	123.1	129.8	119.8

In the ^{13}C NMR spectrum of trichlorophenoxyacet-halogenanilides in chloroform- d_1 signals were observed at 68.97–69.43 and 166.19–166.41 ppm, which were assigned to methylene groups on Ph-O- $\underline{\text{C}}\text{H}_2$ -CO carbon and the carbonyl carbon, respectively. The signals corresponding to phenyl carbons could be observed at 115.52–155.45 ppm.

The discussed organic compounds are colourless substances of melting point 149–230 °C. In the volume of 100 cm³ of solvent at temperature 25 °C they dissoluble 1.0–3.0 g in ethanol, 6.0–13.0 g in acetone and in trace amounts in water (Table 3). These compounds, while having a large molecular mass (between 348–433 g/mole) characterize considerable solubility in acetone and ethanol.

Tab. 8. Phytocidal activity of some trichlorophenoxyacet-halogenanilides in of screening test.

Bioindicator	Compound no.								
	1	2	3	4	8	9	10	11	12
<i>Lolium perenne</i>	2* 0**	2 0	3 1	2 1	1 0	2 1	2 0	1 0	2 1
<i>Avena sativa</i>	2 1	2 0	3 2	3 1	1 1	2 1	2 0	2 1	3 0
<i>Zea mays</i>	2 1	2 1	2 2	2 1	1 0	1 0	1 1	2 1	2 0
<i>Sinapis alba</i>	2 1	1 0	3 1	3 1	0 0	1 1	2 1	3 1	1 0
<i>Pisum sativum</i>	1 0	1 0	3 2	2 1	1 0	2 0	2 2	3 1	2 0
<i>Phaseolus vulgaris</i>	2 0	1 0	3 1	2 1	0 0	1 0	2 1	2 0	1 0
<i>Cucumis sativus</i>	1 0	1 0	2 1	1 1	1 0	1 1	1 0	1 0	1 0
<i>Linum usitatissimum</i>	2 1	0 0	2 1	1 1	1 0	1 1	1 1	1 0	1 0
<i>Beta vulgaris</i>	1 0	0 0	2 1	2 0	1 1	2 1	1 1	1 0	2 0
<i>Fagopyrum esculentum</i>	1 0	1 0	2 0	1 0	0 0	1 0	1 1	1 0	0 0

Application: (*)preemergency, (**) postemergency.

Phytotoxicity: rating scale ranged from 0 to 4 (0 – no injury, 4 – complete death plant) [13].

Biological screening results.

The chloro-fluoro-anilides derivatives of the trichlorophenoxyacetic 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 phytocidal screen using ten plant bioindicators. Results most active compounds they introduced in the Table 8.

The compounds no 1, 2, 3, 4, 8, 9, 10, 11, and 12 show insignificant biological activity. The highest phytocidal activity have the compounds No. 1, 3, 4, 9, 10, 11, and 12. 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 pre emergence and post emergence applications. The best compounds: 2,4,5-trichlorophenoxyacet-4-chloro-3-trifluoromethylanilide, 2,4,5-trichlorophenoxyacet-3-trifluoromethylanilide and 2,4,5-trichloro-phen-oxyacet-4-fluoroanilide (derivatives No. 3, 4 and 1). good controlled *dico-tyledonous* weed species at the dose 2.5 and 1.25 kg a.i./ ha.

Additionally the series of biological activity tests was conducted to compare the following compounds: 2,4,5-trichlorophenoxyacet-4-fluoroanilide (2,4,5-TFA), 2,4,5-trichlorophenoxyacetic acid (2,4,5T) and salt 4-fluoroaniline with 2,4,5-trichlorophenoxyacetic acid (2,4,5Tx4FA). The most active compound against *dicotyledons* weed species being the halogenanilides derivatives of trichlorophenoxyacetic acids, next the salts and free acids, but halogenanilines showed no herbicidal activity.

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

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CURRICULUM VITAE



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