ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN – POLONIA
VOL. LVI, 19 SECTIO AA 2001

Synthesis, structure and biological activity derivatives of the 2-aryl-3-methylbutanoic acids

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Five 2-aryl-3-methylbutanoic acids were obtained, and subsequently – their derivatives of the ester type, thioesters, as well as amines. The compounds were synthesised during the reaction of acid chlorides with: alcohols, thioalcohols or amines. 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 fungicidal activity characterised the derivatives of 4-nitrobenzyl 2(3-chlorophenyl)-3-methylbutanoate and 4,6-dimethoxy-1.3.5-triazyn-2--yl 2(3-phenoxyphenyl)-3-methylbutanoate.

1. INTRODUCTION

Aryl-alkylenecarboxylic acids and their derivatives show a high biological activity. Most of all, salts of these acids were widely applied in many areas of agriculture, herbicides and fungicides among other things [1-3]. Esters and other derivatives of the phenyl-alkylenecarboxylic acids turned out to be more effective herbicides or fungicides than the acids. Their higher biological activity is related to a better permeability through the outer epidermis of the green parts of plants [3-5]. The actual task for researchers who carry out the investigation of pesticides is to obtain new derivatives of aryl-alkylene acids, characterised by an increased biological activity at a smaller dose of the compounds, which could be used on a mass scale to protect agriculture factories.

Well-known and mass-produced pesticides include, among others: in the group of insecticides, derivatives of phenyl- isopropylalkylenecarboxylic acids

– fenvalerate [α-cyanic-4-phenoxybenzyl 2(4-chlorophenyl)isovalerate] [7,8], mawrik [α-cyanic-4-phenoxybenzyl 2(4-trifluoromethyl-2-chlorophenyl) isovalerate]; in the group of systemic herbicides, derivatives of triazines – sancap [2,4-bis(isopropylamino)-6-ethylthio-1,3,5-trazine]; milogard [2-chloro-4,6-bis(isopropylamino)-1,3,5-triazine]; in the group of contact herbicides, derivatives of anilides - bexton [2-chloro-N-isopropylacetanilide] [5,6].

Pesticides representing various classes have in their structure a characteristic isopropyl group, which is largely responsible for the high biological activity of those compounds. Isopropyl substituent causes asymmetry of carbon atoms in the particles of the pesticides and a considerably higher activity of enantiomers R, compared to enantiomers S. The isopropyl group in question also influences the chemical changes of the particles in the plant-soil-water environment. They much more readily undergo different changes, such as hydrolysis, oxidation, and the resulting metabolites are sometimes several times more active biologically than the initial pesticide compounds. Moreover, in these compounds' the isopropyl group increases permeability through cell – membranes of various plants [5,6].

Much smaller amount of the pure usable form of the pesticides is needed than of pesticides from the phenoxyalkane acids group. For example, the dose of the pure usable form of fenvalerate amounts is approx. 60g per hectare of land surface area [8].

For many years an the Department of Organic Chemistry and Technology of MCS University investigations have been under taken way for finding some new organic compounds of potential biological activity [9-13]. Lately, we concentrated on the synthesis of esters, thioesters and amides derivatives of 2-aryl-3-methylbutanoic acids.

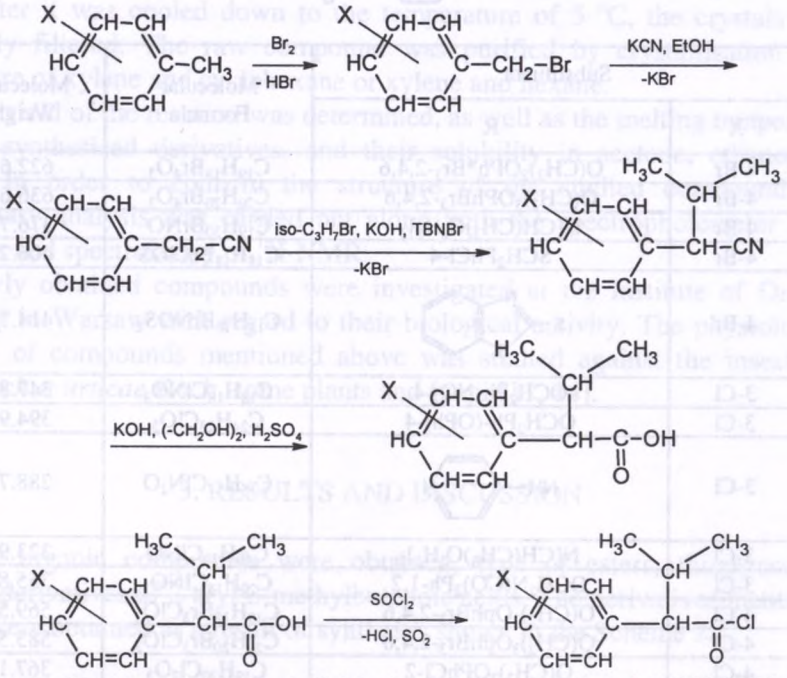
2. EXPERIMENTAL PART

2-Aryl-3-methylbutanoic acids of a structure presented in scheme. At first, a convenient method was elaborated in order to synthesise the 2-aryl-3-methylbutanoic acids using a number of reactions: bromation of aliphatic-aromatic hydrocarbons in the presence of UV radiation; treating potassium cyanide with the obtained benzene bromides; condensation of benzyl cyanides with 2-propyl bromide in potassium hydroxide and tetrabutylamonium bromide.

After the separation and purification, they were hydrolyzed in a ethylene glycol solution of potassium hydroxide at the temperature of 140 °C for 8 hours. Free acids were separated from the reaction mixture by adding a 10%

water solution of sulfuric acid. Raw acids were purified by means of silica gel chromatography, using xylene - dichloromethane – ethyl alcohol mixture.

The course of the reaction whitch produced the derivatives in question is represented in the general Scheme 1.



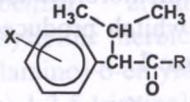
X = 4-Br (No 1), 3-Cl (No 2), 4-Cl (No 3), 3-C_6H_5O (No 4) and 4-C_6H_5O (No 5).

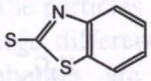
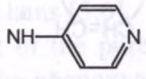
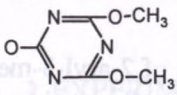
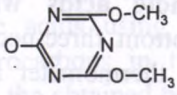
Scheme 1. Chlorides of 2-arylyalkylene acids were obtained in the reaction of the acids with an excess of thionyl chloride

Esters, thioesters and amides derivatives of 2-aryl-3-methylbutanoic acids were synthesised in the reaction of corresponding acid chlorides with alcohols, thioalcohols or amines in the presence of triethylamine in benzene.

Derivatives of 2-aryl-3-methylbutanoic acids with of the structure presented in Table 1. In a round bottom three-necked flask of 250 cm^3. equipped with a mechanical stirrer, a thermometer and a dropping funnel, 0.03 mole of alcohols, thioalcohols or amines and 3.0g (4.1 ml; 0.03 mole) of triethylamine and 50 cm^3 of dry benzene was placed. While stirring the contents of the flask, a solution of 0.02 mole of a corresponding acid chloride was dropped into it in 100 cm^3 of dry benzene during 30 minutes, keeping the temperature within the range of 18-25 °C. While carrying out the reaction, fine colorless crystals of triethylamine hydrochloride started to set out.

Tab. 1. Structure of derivatives of the 2-aryl-3-methylbutanoic acids (1a-5b)



No	Substituent		Molecular Formula	Molecular Weight
	X	R		
1a	4-Br	$O(CH_2)_2OPh^*Br_3$-2,4,6	$C_{19}H_{18}Br_4O_3$	622.62
1b	4-Br	$O(CH_2)_3OPhBr_3$-2,4,6	$C_{20}H_{20}Br_4O_3$	636.63
1c	4-Br	$N[CH(CH_3)C_2H_5]_2$	$C_{19}H_{30}BrNO$	376.74
1d	4-Br	SCH_2PhCl-4	$C_{18}H_{18}BrClOS$	406.25
1e	4-Br		$C_{18}H_{18}BrNOS_2$	414.73
2a	3-Cl	OCH_2Ph-NO_2-4	$C_{18}H_{18}ClNO_4$	347.80
2b	3-Cl	OCH_2Ph-(OPh)-4	$C_{24}H_{23}ClO_3$	394.90
2c	3-Cl		$C_{16}H_{17}ClN_2O$	288.78
2d	3-Cl	$N[CH(CH_3)C_2H_5]_2$	$C_{19}H_{30}ClNO$	323.91
2e	3-Cl	$OCH_2N(CO)_2Ph$-1,2	$C_{20}H_{18}ClNO_3$	355.83
3a	4-Cl	$O(CH_2)_2OphBr_3$-2,4,6	$C_{19}H_{18}Br_3ClO_3$	569.58
3b	4-Cl	$O(CH_2)_3OphBr_3$-2,4,6	$C_{20}H_{20}Br_3ClO_3$	583.50
3c	4-Cl	$O(CH_2)_2OPhCl$-2	$C_{19}H_{20}Cl_2O_3$	367.14
3d	4-Cl	$N[CH(CH_3)C_2H_5]_2$	$C_{19}H_{30}ClNO$	323.91
3e	4-Cl	SCH_2PhCl-4	$C_{18}H_{18}Cl_2OS$	353.18
3f	4-Cl	SCH_2PhCl-2	$C_{18}H_{18}Cl_2OS$	353.18
4a	3-C_6H_5O		$C_{22}H_{23}N_3O_5$	409.45
4b	3-C_6H_5O	$OCH_2N(CO)_2Ph$-1,2	$C_{26}H_{23}NO_5$	429.48
4c	3-C_6H_5O	$O(CH_2)_2OPhCl$-2	$C_{25}H_{25}ClO_4$	424.93
5a	4-C_6H_5O	OCH_2Ph-(OPh)-3	$C_{30}H_{28}O_4$	452.56
5b	4-C_6H_5O		$C_{22}H_{23}N_3O_5$	409.45
5c	4-C_6H_5O	$OCH_2Ph(CH_3)_2$-4,6-(CH_2Cl)-2	$C_{27}H_{29}ClO_3$	436.98

[*] Ph = 

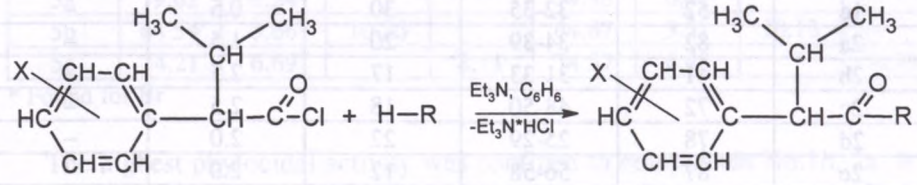
After the whole amount of acid chloride was added to the reaction mixture, the whole was stirred for another 3 hours at a temperature of 35-45 °C. The crystals were filtered and washed with dry warm benzene. Then the solution was concentrated under diminished pressure while heating in the boiling water bath and, after it was cooled down to the temperature of 5 °C, the crystals were carefully filtered. The raw compound was purified by crystallisation from a mixture of xylene and cyclohexane or xylene and hexane.

The yield of the reaction was determined, as well as the melting temperature of the synthesised derivatives, and their solubility in acetone, ethanol and water. In order to confirm the structure of the studied compounds, an elementary analysis was carried out along with the spectrophotometer FTIR analysis and spectroscopy of ^{1}H-NMR.

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 [11, 14].

3. RESULTS AND DISCUSSION

New organic compounds were obtained, type of esters, thioesters and amides derivatives of 2-aryl-3-methylbutanoic acids. The derivatives mentioned above were obtained as a result of syntheses shown in the Scheme 2.



Scheme 2. X and R presented in Table 1

Data concerning the structure of these compounds, the yield of reaction, the melting point and their solubility in three basic solvents were presented in Tables 1, 2.

The structures of the synthesised molecules of the derivatives of 2-aryl-3--methylbutanoic acids are confirmed by a very good agreement of the results of elementary analysis and the calculated contents of C, H, N atoms and the presence of characteristic peaks of absorption bands in the spectres in infrared FTIR and the values of the magne tic proton resonance ^{1}H-NMR. The results are presented in Tables 3, 4 and 5.

The discussed organic compounds are colourless substances of the melting temperature in the range of 29-100 °C. In the volume of 100 cm^3 of solvent at temperature 25 °C they dissolve in amount of 0.5-14.0 g in ethanol, 9-80 g in acetone and only in trace amounts in water. These compounds, while having a relatively large molecule, and so large molecular weight (some 320-630 g/mole) are characterised by a considerable solubility in acetone and ethanol.

The biological research which was carried out testifies to a high or medium biological activity of the compounds in question. Derivatives of 2-aryl-3-methylbutanoic acids showed no insecticidal or acaricidal activity. The most interesting activity was noticed in phytocidal screen using ten plant bioidicators. The data are presented in Table 7.

Tab. 2. Yield of reaction, melting point and solubility of derivatives of the 2-aryl-3--methyl-butanoic acids

No Comp.	Yield (wt.-%)	Melt. point (°C)	Solubility (g/100 cm^3)		
			Acetone	Ethanol	Water
1	2	3	4	5	6
1a	96	55-57	40	1.5	–
1b	93	44-46	80	1.6	–
1c	76	45-47	40	2.0	–
1d	58	98-99	16	0.5	–
1e	52	32-35	30	0.5	–
2a	82	34-39	20	1.5	–
2b	41	31-33	17	2.5	–
2c	72	48-50	18	2.5	–
2d	78	25-29	22	2.0	–
2e	87	56-58	12	2.0	–
3a	92	42-44	38	2.0	–
3b	88	36-37	59	2.5	–
3c	92	27-31	74	14.5	–
3d	73	37-39	27	2.2	–
3e	80	95-96	22	0.5	–
3f	78	30-33	41	1.5	–
4a	69	37-39	10	1.0	–
4b	89	31-33	14	2.0	–
4c	47	36-38	22	3.0	–
5a	55	35-37	18	1.5	–
5b	63	39-41	9	1.0	–
5c	80	29-34	19	2.0	–

Tab. 3. Elementary analysis of derivatives of the 2-aryl-3-methylbutanoic acids

No Comp.	Calculated [wt.%]				Found [wt.%]			
	C	H	N	Cl	C	H	N	Cl
1	2	3	4	5	6	7	8	9
1a	36.65	2.91		51.40*	36.41	3.05		51.01*
1b	37.73	3.17		50.28*	37.98	3.01		50.82*
1c	60.58	8.03	3.72		60.68	7.89	3.51	
1d	53.20	4.43			53.12	4.58		
1e	52.13	4.37	3.38	19.27*	52.01	4.51	2.98	19.03
2a	62.16	5.22	4.03		62.38	5.12	4.35	
2b	73.00	5.87		8.98	72.62	5.94		9.30
2c	66.55	5.93	9.70		66.39	6.13	9.73	
2d	70.46	9.34	4.32		70.22	9.44	4.43	
2e	67.51	5.10	3.94		67.73	5.04	4.02	
3a	40.06	3.16			40.32	2.98		
3b	41.13	3.43			40.74	3.71		
3c	62.16	5.49		19.34	62.31	5.29		19.80
3d	70.49	9.34	4.33		70.59	9.19	4.28	
3e	61.22	5.14		20.11	61.41	5.02		20.31
3f	61.22	5.14		20.11	61.03	5.23		20.37
4a	64.54	5.66	10.26		64.31	5.79	9.97	
4b	72.71	5.40	3.26		72.57	5.51	3.58	
4c	70.67	5.93		8.34	70.51	5.98		8.61
5a	79.62	6.24			79.98	6.01		
5b	64.54	5.66	10.26		64.67	5.51	10.13	
5c	74.21	6.69		8.11	74.57	6.48		8.58

* Found for Br

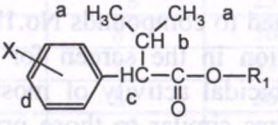
The highest phytocidal activity was confined to compounds No.1b, 2a, b, c, 5a and 5b. They were selected for evaluation in the screen for herbicidal activity. The results confirmed medium herbicidal activity of most of them. Chemicals No 4a, 4b and 5a caused symptoms similar to those produced by phenoxy-alkylene acids class of herbicides after pre- and post emergence applications.

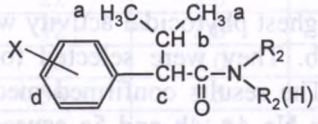
The compounds showed good and medium fungicidal potency against *Erysiphe graminis* of biological activity. Results are presented in Table 7 and in Figure 1. The highest fungicidal activity characterized compounds No 2a, 4a and 5b in Table 1.

Tab. 4. IR analysis of derivatives of the 2-aryl-3-methylbutanoic acids (1a-5b). [Apparatus: spectrophotometer Perkin Elmer model 1725X; KBr; ν (cm^{-1})]

No	Ph-H	CH_3,CH_2	C=O	$CH(CH_3)_2$	O–CH	Ar	C=N
1	2	3	4	5	6	7	8
1a	3075, 3020	2964, 2870	1724	1385, 1370	1265, 1150	1584, 1486	–
1b	3075, 3020	2964, 2874	1726	1385, 1368	1264, 1147	1584, 1486	–
1c	3075, 3020	2964, 2974	1696	1383, 1370	–	1584, 1486	–
1d	3075, 3020	2964, 2974	1719	1385, 1367	–	1585, 1486	–
1e	3075, 3020	2964, 2874	1717	1385, 1367	–	1584, 1486	1584, 1486
2a	3075, 3020	2962, 2872	1721	1380, 1370	1270, 1146	1581, 1485	–
2b	3075, 3021	2962, 2872	1720	1380, 1370	1275, 1078	1581, 1487	–
2c	3075, 3021	2962, 2872	1685	1380, 1366	–	1581, 1486	1581, 1486
2d	3075, 3021	2962, 2872	1697	1385, 1370	–	1581, 1486	–
2e	3075, 3020	2962, 2872	1721	1380, 1365	1260, 1151	1581, 1484	–
3a	3075, 3018	2964, 2876	1724	1385, 1369	1265, 1151	1580, 1487	–
3b	3075, 3020	2964, 2876	1726	1385, 1369	1265, 1146	1580, 1487	–
3c	3075, 3020	2964, 2874	1720	1385, 1369	1260, 1151	1581, 1486	–
3d	3071, 3022	2962, 2876	1697	1383, 1370	–	1580, 1486	–
3e	3075, 3020	2964, 2874	1720	1385, 1367	–	1580, 1486	–
3f	3073, 3021	2963, 2875	1716	1385, 1367	–	1581, 1486	–
4a	3075, 3018	2960, 2871	1718	1380, 1369	1240, 1140	1587, 1485	1587, 1485
4b	3075, 3020	2960, 2871	1721	1380, 1368	1260, 1151	1587, 1485	–
4c	3073, 3022	2961, 2872	1725	1381, 1371	1252, 1147	1587, 1485	–
5a	3075, 3018	2958, 2869	1725	1382, 1365	1275, 1079	1587, 1484	–
5b	3075, 3020	2959, 2872	1719	1380, 1366	1240, 1142	1587, 1484	1587, 1484
5c	3075, 3020	2961, 2873	1723	1382, 1373	1260, 1151	1587, 1485	–

Tab. 5. Spectroscopy of ^{1}H-NMR of derivatives of the 2-aryl-3-ethylbutanoic acids (1a-5b). [Apparatus: spectrophotometer TESLA BS 567 A, 100 MHz; ($CDCl_3$; δ in ppm)].





No Comp.	$(C\underline{H}_3)_2CH$ (a)	$(CH_3)_2C\underline{H}$ (b)	$CHC\underline{H}$-CO (c)	N-C<u>H</u> S-C<u>H</u>$_2$	O-C<u>H</u>$_2$	Ph-<u>H</u> (d)
1	2	3	4	5	6	7
1a	1.0 d; ^3J=6.7 Hz; 6H	2.5-2.8 m; 1H	3.4 d; ^3J=2.0 Hz; 1H	–	4.1-4.2 t; 4H	7.1-7.5 m; 6H
1b	1.0 d; ^3J=6.7 Hz; 6H	1.8-2.6 m; 3H	3.5 d; ^3J=2.0 Hz; 1H	–	3.8-4.2 m, 4H	7.1-7.6 m; 6H
1c	0.6-0.9 m; 12H	1.2-1.9 m; 11H	3.1 d; ^3J=2.0 Hz; 1H	3.9-4.2 m; 2H	–	6.8-7.4 m; 4H
1d	0.9 d; ^3J=6.7 Hz; 6H	2.4-2.7 m; 1H	3.1 d; ^3J=2.0 Hz; 1H	3.9 s; 2H	–	7.2-7.9 m; 8H

1	2	3	4	5	6	7
1e	0.9 d; ^3J=6.7 Hz; 6H	2.4-2.7 m; 1H	3.1 d; J=2.0 Hz; 1H	–	–	7.3-7.9 m; 8H
2a	1.0 d; ^3J=6.7 Hz; 6H	2.4-2.7 m; 1H	3.5 d; ^3J=2.0 Hz; 1H	–	3.9 s; 2H	6.8-8.1 m; 8H
2b	0.9 d; ^3J=6.7 Hz; 6H	2.4-2.7 m; 1H	3.1 d; ^3J=2.0 Hz; 1H	–	3.9 s; 2H	6.8-7.5 m; 13H
2c	0.9 d; ^3J=6.7 Hz; 6H	1.8-2.1 m; 1H	3.4 d; ^3J=2.0 Hz; 1H	–	–	7.1-8.2 m; 8H
2d	0.6-0.9 m; 12H	1.2-1.9 m; 11H	3.6 d; ^3J=2.0 Hz; 1H	3.9-4.3 m; 2H	–	6.8-7.4 m; 4H
2e	0.9 d; ^3J=6.7 Hz; 6H	2.4-2.8 m; 1H	4.1 d; ^3J=2.0 Hz; 1H	6.3 s 2H	6.3 s 2H	6.7-7.7 m; 8H
3a	1.0 d; ^3J=6.7 Hz; 6H	2.4-2.8 m; 1H	3.4 d; ^3J=2.0 Hz; 1H	–	4.1-4.3 t; 4H	7.1-7.5 m; 6H
3b	1.0 d; ^3J=6.7 Hz; 6H	1.8-2.7 m; 3H	3.5 d; ^3J=2.0 Hz; 1H	–	3.7-4.2 m; 4H	7.1-7.6 m; 6H
3c	1.0 d; ^3J=6.7 Hz; 6H	2.4-2.8 m; 1H	3.4 d; ^3J=2.0 Hz; 1H	–	4.1-4.3 t; 4H	6.8-7.5 m; 8H
3d	0.6-0.9 m; 12H	1.2-1.9 m; 11H	3.2 d; ^3J=2.0 Hz; 1H	3.9-4.3 m; 2H	–	7.7-8.1 m; 4H
3e	0.9 d; ^3J=6.7 Hz; 6H	2.3-2.7 m; 1H	3.0 d; ^3J=2.0 Hz; 1H	3.8 s; 2H	–	7.1-8.0 m; 8H
3f	0.9 d; ^3J=6.7 Hz; 6H	2.3-2.7 m; 1H	3.0 d; ^3J=2.0 Hz; 1H	3.9 s; 2H	–	7.1-7.9 m; 8H
4a	1.0 d; ^3J=6.7 Hz; 6H	2.5-2.7 m; 1H	3.5 d; ^3J=2.0 Hz; 1H	–	3.8 s; 6H	7.0-7.4 m; 9H
4b	1.0 d; ^3J=6.7 Hz; 6H	2.5-2.7 m; 1H	4.3 d; ^3J=2.0 Hz; 1H	6.3 s; 2H	6.3 s; 2H	6.8-7.7 m; 13H
4c	1.0 d; ^3J=6.7 Hz; 6H	2.5-2.8 m; 1H	3.6 d; ^3J=2.0 Hz; 1H	–	4.1-4.4 t; 4H	6.7-7.4 m; 13H
5a	1.0 d; ^3J=6.7 Hz; 6H	2.5-2.7 m; 1H	3.5 d; ^3J=2.0 Hz; 1H	–	3.9 s; 2H	6.9-7.5 m; 18H
5b	1.0 d; ^3J=6.7 Hz; 6H	2.5-2.8 m; 1H	3.5 d; ^3J=2.0 Hz; 1H	–	3.9 s; 2H	7.1 -7.4 m; 9H
5c	1.0 d; ^3J=6.7 Hz; 6H	2.3-2.8 m; 7H	3.5 d; ^3J=2.0 Hz; 1H	4.6 s; 2H	5.9 s; 2H	6.8-7.4 m; 11H

Tab. 6. Phytocidal activity of the derivatives of the 2-aryl-3-methylbutanoic acids in the screening test

Bioindicator	Compound No.										
	1b	2a	2c	2d	2e	3a	3b	4a	4b	5a	5b
Lolium perenne L	0*	0	2	1	2	1	2	2	2	2	2
	0**	0	0	1	1	0	0	0	1	1	0
Avena sativa L	1	0	1	1	2	1	1	1	2	2	1
	0	0	0	0	1	0	0	0	1	1	0
Zea mays L	0	0	1	1	1	0	1	2	1	1	2
	0	0	1	0	1	0	1	0	1	1	0
Sinapis alba L	1	1	1	1	1	1	1	2	1	2	2
	0	0	1	0	1	0	1	1	1	1	1
Pisum sativum L	0	0	1	1	1	0	1	2	1	2	2
	0	0	1	0	1	0	1	2	1	1	2

	1b	2a	2c	2d	2e	3a	3b	4a	4b	5a	5b
Phaseolus vulgaris L	1	0	1	2	1	0	1	2	1	1	2
	0	0	0	1	1	0	0	1	1	0	1
Cucumis sativus L	1	1	1	1	2	0	1	1	2	2	1
	0	0	1	1	1	0	1	1	2	1	1
Linum Usitatissimum L	0	0	1	1	1	1	1	2	1	1	2
	0	0	1	1	1	1	1	1	1	1	1
Beta vulgaris L	0	0	1	1	1	0	1	1	1	0	1
	0	0	1	0	0	0	0	1	0	0	1
Fagopyrum esculentum Moench	1	1	1	1	1	0	1	1	1	2	1
	0	0	1	1	0	0	1	0	1	1	1

Application: * preemergency, ** postemergency
Phytotoxicity: rating scale ranged from 0 to 4 (0 - no injury, 4 - complete death plant) [14].

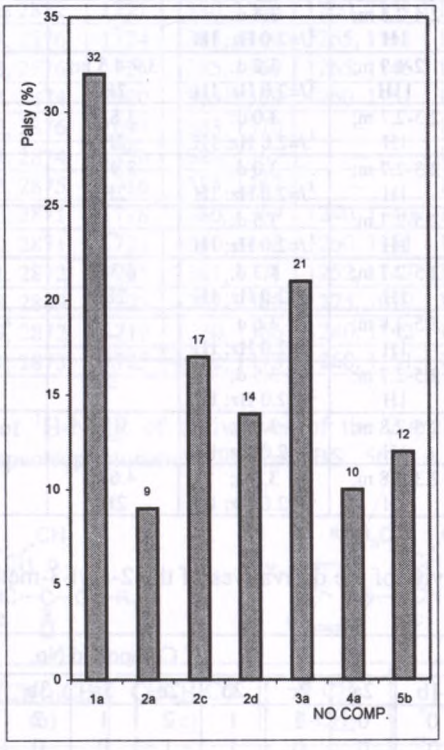


Fig. 1. Fungicidal activity of the derivatives of 2-arylo-3-methylbutanoic acids for *Erysiphe graminis* as a bioindicator

Tab. 7. Insecticidal, acaricidal and fungicidal activity of the derivatives of 2-aryl-3--methyl-butanoic acids

Bioindicator	Compound No.						
	1b	2a	2c	2d	3a	4a	5b
*Musca domestica**	> 25	> 25	> 25	> 25	> 25	> 25	> 25
*Tetranychus urticae***	>0.1	> 0.1	> 0.1	> 0.1	> 0.1	> 0.1	> 0.1
*Alternaria alternata****	>100	>100	>100	>100	>100	>100	>100
*Botrytis cinerea****	>100	>100	>100	>100	>100	>100	>100
*Rhizoctonia solani****	>200	>200	>200	>200	>200	>200	>200
*Fusarium culmorum****	>200	>200	>200	>200	>200	>200	>200
*Phytophthora cactorum****	>200	>200	>200	>200	>200	>200	>200
*Erysiphe graminis*****	32	9	17	14	21	10	12

*Insecticidal activity – concentration (in $\mu g/cm^3$) causing at least a 90% mortality of the bioindicator.

**Acaricidal activity – a dose (in $\mu g/cm^3$) causing at least a 90% mortality of the bioindicator.

***Fungicidal activity – an *in vitro* test, concentration (in $\mu g/cm^3$) causing at least a 90% mortality of the bioindicator.

**** Fungicidal activity – an *in vivo* test (percentage of impact): 25-50 – medium, 5-25 – good [14].

4. CONCLUSIONS

22 new 2-aryl-3-methylbutanoic acid derivatives were obtained. Their chemical structure was confirmed and physico-chemical properties and biological activity were examined. To sum up, the obtained derivatives of aryl--methylbutanoic acids are not insecticides or acaricides, but reveal medium herbicidal activity and high fungicidal activity against *Erysiphe graminis* as a bioindicator.

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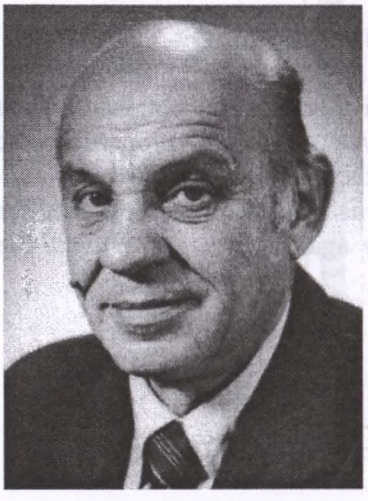
CURRICULA VITAE



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Results of the investigations from these various fields were presented in over 100 scientific national and foreign journals, 60 patents and 50 communications. In 1958 he became member of the Polish Chemical Society and, up to now he has promoted 8 doctoral dissertations and over 200 M. Sc. degrees.

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Results of the investigations from these various fields were presented in over 30 scientific national and foreign journals, 10 patents and 40 communications.