Synthesis and herbicidal activity of 6-(aryloxy-R^1-amido)-2-R^2-thiobenzothiazoles

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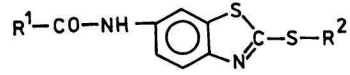
6-(Aryloxy-R^1-amido)-2-R^2-thiobenzothiazoles ($R^1 = CH_2$, $CHCH_3$, R^2 = alkyl C_1—C_8, cyclopentyl, benzyl) were synthesized by the reaction of aryloxyethanoyl or 2-aryloxypropanoyl chlorides with 2-R^2-thio-6--aminobenzothiazoles in the medium of tetrahydrofuran and dimethylformamide in the presence of a tertiary base. Some of prepared compounds highly inhibited the growth of tested plants.

Among benzothiazole compounds Benzothiazurone (1-(2-benzothiazolyl)-3--methylurea) and Methylbenzothiazurone (1-(2-benzothiazolyl)-1,3-dimethylurea) are used as herbicidal agents [1]. 2-Alkylthiobenzothiazoles are known as defoliants; especially Butylcaptax (2-butylthiobenzothiazole) is of use in practice as defoliant in a dose of 10—12 kg ha^{-1} [2, 3]. 6-Benzoylamino-2-alkylthiobenzothiazoles [4—6] and 6-acetamido-2-alkylthiobenzothiazoles [7, 8] show antimicrobial activity. The second reaction component, *i.e.* aryloxyethanoic acids are commonly used as plant-protecting and growth-regulating agents in agricultural practice [1]. As we have reported [9], 6-X-2-(aryloxyacetamido)benzothiazoles (X = H, NO_2, Br, SCN, CH_3) exhibit also a herbicidal activity.

The aim of the present work was to synthesize compounds from both active components and perform their pesticidal tests [10—12]. The acylation was provided using aryloxyacetyl chlorides in a mixture of tetrahydrofuran and dimethylformamide. The yields of products were approximately 80%. Thirty--one new compounds were prepared including nineteen 6-(aryloxyethaneamido)- and twelve 6-(2-aryloxypropaneamido)-2-alkylthiobenzothiazoles. Among 6-amino-2-alkylthiobenzothiazole derivatives representatives were chosen containing a saturated alkyl group (C_1—C_8), allyl group and a cyclopentyl or a benzyl group. From aryloxyalkanecarboxylic acids four compounds possessing pesticidal activity were chosen: (2,4-dichlorophenoxy)ethanoic, 2-(2,4-dichlo-

Table 1

Characterization of the prepared 6-R^1-amido-2-R^2-thiobenzothiazoles



Compound	R^1	R^2	Formula M_r	w_i(calc.)/% w_i(found)/%					M.p. °C
				C	H	Cl	N	S	
I	2-CH_3-4-Cl-C_6H_3-O-CH_2	CH_3	$C_{17}H_{15}ClN_2O_2S_2$ 378.9	53.89 54.05	3.99 4.11	9.35 9.38	7.39 7.45	16.93 17.11	159—160
II	2,4-Cl_2-C_6H_3-O-CH_2	CH_3CH_2	$C_{17}H_{14}Cl_2N_2O_2S_2$ 413.4	49.40 49.61	3.41 3.59	17.15 17.37	6.78 6.89	15.51 15.24	152—154
III	2-CH_3-4-Cl-C_6H_3-O-CH_2	$(CH_3)_2CH$	$C_{19}H_{19}ClN_2O_2S_2$ 406.9	56.08 56.17	4.71 4.63	8.71 8.82	6.88 6.99	15.76 16.09	159—161
IV	2,4-Cl_2-C_6H_3-O-CH_2	$(CH_3)_2CH$	$C_{18}H_{16}Cl_2N_2O_2S_2$ 427.4	50.59 50.38	3.77 3.48	16.59 16.75	6.55 6.72	15.01 15.06	153—155
V	2,4-Cl_2-C_6H_3-O-CH_2	CH_3	$C_{16}H_{12}Cl_2N_2O_2S_2$ 399.4	48.11 48.23	3.03 3.34	17.76 17.85	7.01 7.16	16.05 16.19	193—195
VI	2-CH_3-4-Cl-C_6H_3-O-CH_2	CH_2=CH—CH_2	$C_{19}H_{17}ClN_2O_2S_2$ 404.9	56.36 56.54	4.23 4.46	8.75 9.05	6.92 6.81	15.84 15.86	140—143
VII	2-CH_3-4-Cl-C_6H_5-O-CH_2	$(CH_3)_2CHCH_2$	$C_{20}H_{21}ClN_2O_2S_2$ 420.9	57.06 57.18	5.03 5.21	8.42 8.58	6.65 6.49	15.23 15.56	135—137
VIII	2,4-Cl_2-C_6H_3-O-CH_2	$CH_3(CH_2)_2CH_2$	$C_{19}H_{18}Cl_2N_2O_2S_2$ 441.4	51.70 51.92	4.11 4.29	16.06 16.31	6.35 6.54	14.54 14.54	129—132
IX	2-CH_3-4-Cl-C_6H_3-O-CH_2	$CH_3(CH_2)_2CH_2$	$C_{20}H_{21}ClN_2O_2S_2$ 420.9	57.06 57.19	5.03 5.12	8.42 8.55	6.65 6.41	15.23 15.32	151—153
X	2,4-Cl_2-C_6H_3-O-CH_2	$(CH_2)_4CH$	$C_{20}H_{18}Cl_2N_2O_2S_2$ 453.4	52.98 53.14	4.00 4.11	15.64 15.78	6.18 6.25	14.14 14.26	132—134

Table 1 (Continued)

Compound	R^1	R^2	Formula M_r	w_i(calc.)/% w_i(found)/%					M.p. °C
				C	H	Cl	N	S	
XI	2-CH_3-4-Cl-C_6H_3-O-CH_2	$(CH_2)_4CH$	$C_{21}H_{19}ClN_2O_2S_2$ 430.9	58.53 58.62	4.44 4.46	8.23 8.48	6.50 6.63	14.88 15.07	156—158
XII	2,4-Cl_2-C_6H_3-O-CH_2	$CH_3(CH_2)_4CH_2$	$C_{21}H_{22}Cl_2N_2O_2S_2$ 469.4	53.73 53.96	4.72 4.93	15.10 15.27	5.97 5.82	13.66 13.85	104—105
XIII	2-CH_3-4-Cl-C_6H_3-O-CH_2	$CH_3(CH_2)_4CH_2$	$C_{22}H_{25}ClN_2O_2S_2$ 449.0	58.85 58.62	5.61 5.42	7.89 7.89	6.24 6.42	14.28 13.98	143—145
XIV	2-CH_3-4-Cl-C_6H_3-O-CH_2	$C_6H_5CH_2$	$C_{23}H_{19}ClN_2O_2S_2$ 455.0	60.72 60.54	4.21 4.38	7.79 7.86	6.16 6.23	14.09 14.09	210—212
XV	2,4-Cl_2-C_6H_3-O-CH_2	$C_6H_5CH_2$	$C_{22}H_{16}Cl_2N_2O_2S$ 475.42	55.58 55.74	3.39 3.48	14.91 14.98	5.89 5.71	13.49 13.52	196—197.5
XVI	2-CH_3-4-Cl-C_6H_3-O-CH_2	$CH_3(CH_2)_5CH_2$	$C_{23}H_{27}ClN_2O_2S_2$ 463.1	59.66 59.86	5.88 5.74	7.66 7.75	6.05 6.12	13.85 14.00	143—144
XVII	2,4-Cl_2-C_6H_3-O-CH_2	$CH_3(CH_2)_6CH_2$	$C_{23}H_{26}Cl_2N_2O_2S_2$ 497.5	55.53 55.71	5.27 5.36	14.25 14.33	5.63 5.75	12.89 12.93	108—112
XVIII	2-CH_3-4-Cl-C_6H_3-O-CH_2	$CH_3(CH_2)_6CH_2$	$C_{24}H_{29}ClN_2O_2S_2$ 477.1	60.42 60.51	6.13 6.24	7.43 7.59	5.87 6.03	13.44 13.54	137—138
XIX	3-CH_3-C_6H_4-O-CH_2	$CH_3(CH_2)_6CH_2$	$C_{24}H_{30}N_2O_2S_2$ 442.6	65.12 65.38	6.78 6.74	— —	6.32 6.39	14.46 14.44	110—112
XX	2-CH_3-4-Cl-C_6H_3-O-CH-CH_3	CH_3	$C_{18}H_{17}ClN_2O_2S_2$ 392.9	55.18 55.18	4.36 4.43	9.02 9.10	7.13 7.18	16.32 16.30	172—176
XXI	2,4-Cl_2-C_6H_3-O-CH-CH_3	CH_3CH_2	$C_{18}H_{16}Cl_2N_2O_2S_2$ 427.4	50.59 50.42	3.77 3.51	16.59 16.53	6.55 6.36	15.00 15.25	160—162
XXII	2-CH_3-4-Cl-C_6H_3-O-CH-CH_3	CH_3CH_2	$C_{19}H_{19}ClN_2O_2S_2$ 406.9	56.08 56.29	4.71 4.56	8.71 8.73	6.88 6.74	15.76 16.00	141· -143
XXIII	2,4-Cl_2-C_6H_3-O-CH_2	CH_2=CH—CH_2	$C_{18}H_{14}Cl_2N_2O_2S_2$ 425.4	50.82 50.66	3.32 3.28	16.66 16.90	6.58 6.31	15.07 15.31	134—136
XXIV	2-CH_3-4-Cl-C_6H_3-O-CH-CH_3	CH_2=CH—CH_2	$C_{20}H_{19}ClN_2O_2S_2$ 418.9	57.34 57.61	4.54 4.72	8.46 8.71	6.69 6.84	15.31 15.15	135—138

Table 1 (Continued)

Compound	R^1	R^2	Formula M_r	w_i(calc.)/% w_i(found)/%					M.p. °C
				C	H	Cl	N	S	
XXV	2-CH_3-4-Cl-C_6H_3-O-CH-CH_3	$CH_3(CH_2)_2CH_2$	$C_{21}H_{21}ClN_2O_2S_2$ 432.9	58.25 58.45	4.89 4.98	8.19 8.27	6.47 6.63	14.81 14.81	132—134
XXVI	2,4-Cl_2-C_6H_3-O-CH-CH_3	$CH_3(CH_2)_2CH_2$	$C_{20}H_{20}Cl_2N_2O_2S_2$ 455.4	52.75 52.83	4.43 4.62	15.57 15.54	6.15 6.24	14.08 14.15	105—107
XXVII	2,4-Cl_2-C_6H_3-O-CH-CH_3	$CH_3(CH_2)_4CH_2$	$C_{22}H_{24}Cl_2N_2O_2S_2$ 483.5	54.65 54.79	5.00 5.23	14.67 14.68	5.79 5.88	13.26 13.25	102—104
XXVIII	2-CH_3-4-Cl-C_6H_3-O-CH-CH_3	$CH_3(CH_2)_4CH_2$	$C_{23}H_{27}Cl_2N_2O_2S_2$ 463.1	59.66 59.86	5.88 6.09	7.66 7.86	6.05 6.14	13.85 13.97	117—118
XXIX	2,4-Cl_2-C_6H_3-O-CH-CH_3	$C_6H_5CH_2$	$C_{23}H_{18}Cl_2N_2O_2S_2$ 489.4	56.44 56.62	3.71 3.86	14.49 14.64	5.72 5.95	13.10 13.20	168—169
XXX	2-CH_3-4-Cl-C_6H_3-O-CH-CH_3	$C_6H_5CH_2$	$C_{24}H_{21}ClN_2O_2S_2$ 469.0	61.46 61.68	4.51 4.38	7.56 7.56	5.97 6.21	13.67 13.92	167—169
XXXI	2,4-Cl_2-C_6H_3-O-CH-CH_3	$CH_3(CH_2)_6CH_2$	$C_{24}H_{28}Cl_2N_2O_2S_2$ 511.5	56.35 56.48	5.52 5.36	13.86 13.83	5.48 5.65	12.54 12.36	86—89

rophenoxy)propanoic, (2-methyl-4-chlorophenoxy)ethanoic, and 2-(2-methyl--4-chlorophenoxy)propanoic acids. In only case for preparation of compound *XIX* (see Table 1) the inactive (3-methylphenoxy)ethanoic acid was used.

All 31 compounds were tested for herbicidal activity using the following model plants: *Avena sativa, Panicum miliaceum, Fagopyrum vulgare, Lepidium sativum*, and *Sinapis alba*. Among the tested plants only *Fagopyrum vulgare, Lepidium sativum*, and *Sinapis alba* are sensitive to the prepared compounds. A 100% inhibitory activity is exhibited only by three compounds, *i.e.* compound *IV* containing an isopropyl group attached to the sulfur as well as a 2,4-dichlorophenoxyethanoyl group on the nitrogen and compounds *XXIII* and *XXIV* with an allyl group on the sulfur and 2,4-dichlorophenoxyethanoyl or 2-(2-methyl-4-chlorophenoxy)propanoyl group on the nitrogen. The cyclopentyl derivative of 2-thio-6-(2-methyl-4-chlorophenoxyethaneamido)benzothiazole (*XI*) appeared to be very active, causing 90% growth-inhibition of the above-mentioned plants. The activity turns out using doses of 2.5 kg ha^{-1} at the postemergent application. The dose of 2.5 kg ha^{-1} at the preemergent application was found to be active only for compound *XXIV* tested on *Lepidium sativum*. The herbicidal tests showed that the compounds (see Table 3) are active especially at the postemergent growth of wide-leaf plants. The starting 6-amino--2-alkylthiobenzothiazole was found to be herbicidally inactive.

The ^1H NMR spectra of prepared compounds confirmed their structure. The signals of protons have positions and multiplicities corresponding to their surroundings. The methylene group of aryloxymethyleneacyl moiety exhibits a singlet in the region of $\delta = 4.52$—4.80. The changes in positions of signals were observed in dependence on solvents used. The samples measured in deuterated chloroform exhibit a singlet at $\delta = 4.5$. In the case of compounds containing chlorine attached to 2-aryloxy group the positions of signals are shifted to lower field by $\delta = 0.10$—0.15. The signal of the methine group proton of 2-aryloxypropanoyl moiety is observed as a quadruplet in the region of $\delta = 4.47$—5.00. The methyl group proton of the same moiety is represented by a doublet in the range of $\delta = 1.32$—1.65.

The signals of protons of the methyl group attached in position 2 of the aryloxy moiety were found as singlets in the region of $\delta = 2.15$—2.25. The methyl group attached to the sulfur in the position 2 of the benzothiazole skeleton exhibits a singlet signal in the lower-field region of $\delta = 2.65$—2.68.

The methylene group of higher alkyl moieties attached directly to the sulfur atom in the position 2 of the benzothiazole ring can be easily distinguished from other methylene groups, because it exhibits signals in the region of $\delta = 3.10$ —3.40 as a quadruplet (compound *XXII*), or a triplet (compounds *VIII, IX, XIII, XVII—XIX, XXVI—XXVIII, XXXI*), or a doublet (in the case of compound *VII*). In allyl-substituted derivatives (*VI, XXIII, XXIV*) the signals of

Table 2

^{1}H NMR spectra of the prepared compounds

Compound	Solvent	δ
I	DMSO	2.15 (s, 3H); 2.65 (s, 3H); 4.62 (s, 2H); 6.70—7.90 (m, 5H); 8.27 (s, 1H); 10.03—10.11 (s, 1H)
III	DMSO	1.24—1.47 (d, 6H); 2.15 (s, 3H); 2.74—3.05 (m, 1H); 4.65 (s, 2H); 6.68—7.19 (m, 3H); 7.37—7.78 (m, 2H); 8.16—8.35 (m, 1H); 10.07—10.50 (s, 1H)
IV	DMSO	1.37 (d, 6H, J = 4 Hz); 3.81—4.12 (s, 1H); 4.78 (s, 2H); 6.95—7.77 (m, 5H); 8.27 (s, 1H)
V	DMSO	2.68 (s, 3H); 4.77 (s, 2H); 7.00—7.78 (m, 5H); 8.10—8.36 (s, 1H); 9.32—9.73 (s, 1H)
VI	$CDCl_3$	2.27 (s, 3H); 3.92 (d, 2H, J = 4 Hz); 4.47 (s, 2H); 5.02—5.50 (t, 2H); 5.75—6.02 (m, 1H); 6.56—7.35 (m, 3H); 7.65—7.85 (m, 1H); 8.27 (s, 1H)
VII	$CDCl_3$	0.90—1.20 (d, 6H); 1.40—1.90 (m, 1H); 2.30 (s, 3H); 3.20 (d, 2H, J = 3 Hz); 4.52 (s, 2H); 6.63—7.93 (m, 5H); 8.21—8.37 (s, 1H); 10.40—10.87 (s, 1H)
VIII	DMSO	0.75—1.07 (t, 3H); 1.27—1.90 (m, 4H); 3.12—3.45 (t, 2H); 4.80 (s, 2H); 6.93—7.78 (m, 5H); 8.27 (s, 1H); 10.17—10.71 (s, 1H)
IX	DMSO	0.73—1.00 (t, 3H); 1.15—1.93 (m, 4H); 2.22 (s, 3H); 3.08—3.43 (t, 2H); 4.63 (s, 2H); 6.66—7.81 (m, 5H); 8.27 (s, 1H); 10.03—10.56 (s, 1H)
X	$CDCl_3$	1.45—2.25 (m, 8H); 3.87—4.23 (s, 1H); 4.50 (s, 2H); 6.67—7.88 (m, 5H); 8.27 (s, 1H); 8.42—8.81 (m, 1H)
XI	DMSO	1.575 (s, 4H); 2.14 (s, 3H); 3.27 (s, 4H); 3.75—4.22 (s, 1H); 6.67—7.21 (m, 3H); 7.31—7.80 (m, 2H); 8.27 (s, 1H); 10.05—10.36 (s, 1H)
XIII	$CDCl_3$	0.76—1.01 (t, 3H); 1.15—1.92 (m, 6H); 2.25 (s, 3H); 3.07—3.42 (t, 2H); 4.50 (s, 2H); 6.55—7.87 (m, 5H); 8.16—8.47 (d, 2H); 10.40—10.80 (m, 1H)
XV	DMSO	4.51 (s, 2H); 4.77 (s, 2H); 6.87—7.82 (m, 5H); 8.25 (s, 1H)
XVI	DMSO	1.00—1.34 (t, 3H); 2.37 (s, 3H); 2.92—3.37 (s, 12H); 4.65 (s, 2H); 6.68—7.77 (m, 5H); 8.27 (s, 1H); 10.13—10.51 (m, 1H)
XVII	$CDCl_3$	0.67—0.97 (t, 3H); 1.10—1.52 (m, 8H); 1.65—2.15 (m, 4H); 3.17—3.45 (t, 2H); 4.55 (s, 2H); 6.70—7.92 (m, 5H); 8.25—8.40 (s, 1H); 8.45—8.82 (t, 1H)
XVIII	$CDCl_3$	0.82 (m, 3H); 1.07—1.52 (m, 10H); 1.62—1.97 (m, 2H); 2.25 (s, 3H); 3.12—3.37 (t, 2H); 4.48 (s, 2H); 6.56—7.91 (m, 5H); 8.25—8.37 (s, 1H); 10.42—10.70 (s, 1H)
XIX	$CDCl_3$	0.82 (m, 3H); 1.08—1.52 (m, 10H); 1.65—1.97 (m, 2H); 2.27 (s, 3H); 3.13—3.40 (t, 2H); 4.54 (s, 2H); 6.64—7.85 (m, 6H); 8.20—8.48 (m, 2H)
XX	$CDCl_3$	1.53 (d, 3H, J = 3 Hz); 2.27 (s, 3H); 2.66 (s, 3H); 4.47—4.85 (q, 1H); 6.61—7.92 (m, 5H); 8.17—8.37 (s, 1H); 10.30—10.62 (m, 1H)

Table 2 (Continued)

Compound	Solvent	δ
XXII	DMSO	1.25—1.62 (t, 3H); 2.20 (s, 3H); 3.12—3.35 (q, 2H); 4.62—4.93 (q, 1H); 6.58—7.77 (m, 5H); 8.17—8.37 (s, 1H); 9.50—10.37 (s, 1H)
XXIII	DMSO	3.87 (d, 2H, J = 4 Hz); 4.75 (s, 2H); 4.92—5.47 (t, 2H); 5.65—6.17 (m, 1H); 6.91—7.78 (m, 5H); 8.15—8.30 (s, 1H); 10.00—10.30 (d, 1H)
XXIV	DMSO	1.165—1.37 (d, 3H); 2.17 (s, 3H); 3.75—4.09 (d, 2H); 4.57—4.95 (q, 1H); 5.00—5.46 (t, 2H); 5.62—5.87 (m, 1H); 6.57—7.18 (m, 3H); 7.38—7.80 (m, 2H); 8.21—8.37 (s, 1H); 10.00—10.45 (m, 1H)
XXV	DMSO	0.75—0.95 (t, 3H); 1.52 (d, 3H, J = 3 Hz); 2.18 (s, 3H); 3.10—3.51 (m, 6H); 4.65—5.00 (q, 1H); 6.66—7.80 (m, 5H); 8.27 (s, 1H)
XXVI	DMSO	0.61—0.95 (t, 3H); 1.02—1.78 (m, 4H); 1.52 (d, 3H, J = 3 Hz); 3.00—3.37 (t, 2H); 4.67—5.06 (q, 1H); 6.88—7.87 (m, 5H); 8.27 (s, 1H); 10.12—10.50 (m, 1H)
XXVII	$CDCl_3$	0.68—1.00 (t, 3H); 1.12—2.13 (m, 11H); 3.275 (t, 2H, J = 6 Hz); 4.65—4.90 (q, 1H); 6.76—7.93 (m, 5H); 8.25—8.50 (s, 1H); 10.37—10.67 (m, 1H)
XXVIII	$CDCl_3$	0.75—1.06 (t, 3H); 1.25—1.48 (d, 3H); 1.42—2.18 (m, 8H); 2.30—2.45 (s, 3H); 3.20—3.46 (t, 2H); 4.51—4.87 (m, 1H); 6.66—7.81 (m, 6H); 8.15—8.48 (s, 1H)
XXIX	DMSO	1.55 (d, 3H, J = 3 Hz); 4.50 (s, 2H); 4.70—4.96 (q, 1H); 6.87—7.82 (m, 10H); 8.30 (s, 1H); 10.15—10.5 (m, 1H)
XXX	DMSO	1.50 (d, 3H, J = 4 Hz); 2.16 (s, 3H); 4.51 (s, 2H); 4.65—4.90 (q, 1H); 6.61—7.81 (m, 10H); 8.13—8.34 (s, 1H); 10.12—10.55 (m, 1H)
XXXI	$CDCl_3$	0.72—0.96 (t, 3H); 1.14—1.47 (m, 6H); 1.59—1.91 (m, 6H); 3.20—3.44 (t, 2H); 4.63—4.93 (q, 1H); 6.78—7.87 (m, 5H); 8.32 (s, 2H); 8.63—8.84 (s, 1H)

6-Amino-2-ethylthiobenzothiazole (*XXXII*): 1.21—1.42 (t, 3H); 2.99—3.32 (q, 2H); 5.15 (s, 2H); 6.60—6.98 (m, 2H); 7.58 (s, 1H).

methylene group can be observed as a doublet at the values of $\delta = 3.70$—4.07. In the spectra of 2-thiobenzoyl derivatives (*XIV*, *XV*, *XXIX*), the signals of CH_2 group protons can be found at $\delta = 4.5$, which is very close to the value of signal belonging to CH_2 protons of aryloxymethyleneacyl group. The assignment in the case of compounds *XXIX* and *XXX* was made on the basis of absence of the higher-field singlet ($\delta = 4.65$—4.70) and the presence of a quadruplet with an integral corresponding to one hydrogen atom. The signal of methine group proton of compounds *III* and *IV* occurs as a broader singlet, in which the multiplicity in the region of $\delta = 3.70$—4.12 cannot be distinguished. Similarly in the case of 2-cyclopentylthio derivatives the signal of the methine group is observed in the region of $\delta = 3.75$—4.22. The methine group of allyl derivatives exhibits a multiplet in the range of $\delta = 5.65$—6.10. The signal of terminal methylene group of allyl derivatives (*VI*, *XXIII*, and *XXIV*) occurs in the spectra as an asymmetric triplet in the region of $\delta = 4.90$—5.40.

The signals of aromatic protons of all prepared compounds were found in the region over $\delta = 6.5$. A well distinguished signal of one of the aromatic protons occurs as a singlet at high values of δ in the range of 8.16—8.46. We assigned this signal to the proton in position 7 of benzothiazole skeleton. A similarly distinguished singlet was also observed in the case of compound *XXXII*, but in the higher-field region at $\delta = 7.35$. The signals of remaining aromatic protons occur as multiplets in the range of $\delta = 6.50$—7.90. In most of spectra the signal of amide group proton was found in the region of $\delta = 10.05$—10.36 as a broad singlet.

Experimental

The ^{1}H NMR spectra of prepared compounds were measured on a Tesla BS 487 (80 MHz) spectrometer at 24°C in DMSO or $CDCl_3$ using tetramethylsilane or hexamethyldisiloxane as internal standards (Table 2).

The herbicidal tests were carried out according to [13]. The scale of activity was 0—5, where 0 means healthful, undamaged plants, 5 means the plants died away and 1—4 are the intermediate stages of damage. At the evaluation all significant changes affecting the living ability of tested plants (Table 3) were considered.

6-(Aryloxyethaneamido)-2-R^2-thiobenzothiazoles (I—XIX) and 6-(2-aryloxypropaneamido)-2-R^2-thiobenzothiazoles (XX—XXXI)

6-Amino-2-R^2-thiobenzothiazole (0.01 mol) was dissolved in dimethylformamide (*ca.* 20—30 cm^3) and mixed with aryloxyethanoyl or aryloxypropanoyl chlorides (0.012 mol)

Table 3

Activity of some synthesized compounds at the postemergent (A, dose 2.5 kg ha^{-1}) and preemergent (B, dose 5 kg ha^{-1}) application

Plant	Application	*IV*	*VIII*	*XI*	*XXIII*	*XXIV*	MCPA
Avena	A	0	0	0	0	0	3
sativa	B	0	0	0	0	0	3
Panicum	A	0	0	0	0	0	
miliaceum	B	0	0	0	0	0	2
Fagopyrum	A	3.5	3	4	5	2	4
vulgare	B	0	0	0	0	1	5
Lepidium	A	5	2	4.5	5	5	5
sativum	B	0	0	0	0	5	5
Sinapis	A	4	2.5	4.5	5	5	4
alba	B	1	2.5	0	2	2	5

MCPA = 2-methyl-4-chlorophenoxyethanoic acid.

in tetrahydrofuran (*ca.* 20 cm^3). Pyridine or triethylamine (0.014 mol) was added dropwise during 20 min and the mixture was stirred for 1 h at 40—50°C. The mixture was poured into cool water (50 cm^3) and neutralized by sodium hydrogencarbonate. After 12 h standing the eliminated precipitate was sucked off and recrystallized from the mixture of ethanol and dimethylformamide.

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