Benzothiazole compounds
XXIII. Synthesis, structure, and growth-regulating activity of 2-alkoxycarbonylmethylthio-3-alkylbenzothiazolium salts

[a]V. SUTORIS, [b]A. GÁPLOVSKÝ, [a]R. SOHLEROVÁ, and [c]V. SEKERKA

[a]*Department of Organic Chemistry, Faculty of Natural Sciences, Komenský University, CS-842 15 Bratislava*

[b]*Institute of Chemistry, Komenský University, CS-842 15 Bratislava*

[c]*Department of Molecular Biology and Genetics, Faculty of Natural Sciences, Komenský University, CS-842 15 Bratislava*

Received 13 August 1984

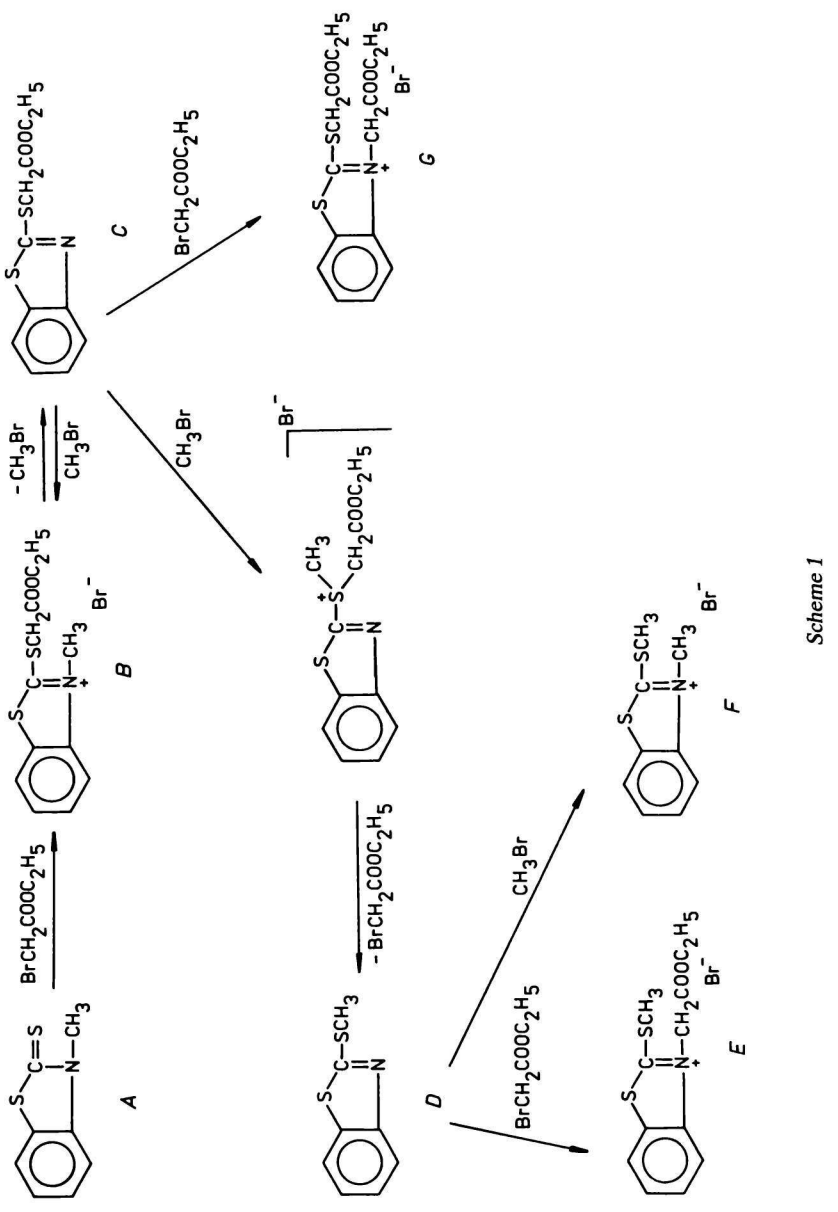
2-Alkoxycarbonylmethylthio-3-alkylbenzothiazolium salts have been prepared by treatment of 3-alkyl-2-benzothiazolinethiones with esters of bromoacetic acid and their structures were proved by evaluation of ^{1}H NMR spectra. It was found that besides 2-alkoxycarbonylmethylthio-3-alkylbenzothiazolium salts as the main product also 2-alkoxycarbonylmethylthiobenzothiazole, 2-alkylthiobenzothiazole, and 2-alkylthio-3-alkoxycarbonylmethylbenzothiazolium bromide were formed, indicating the formation of sulfonium salts as intermediates. The course of the reaction was studied by IR spectroscopy, isotachophoresis as well as by liquid and gas chromatography. 2-Methoxycarbonylmethylthio-3-methylbenzothiazolium bromide was found to show high growth-stimulating activity ($a_{st} = +7.5 \times 10^{-11}$ mol dm^{-3}).

В результате взаимодействия 3-алкил-2-бензотиазолинтионов с эфирами бромуксусной кислоты были получены соли 2-алкоксикарбонилметилтио-3-алкилбензотиазолия и их структуры были доказаны посредством изучения их ^{1}H ЯМР спектров. Найдено, что помимо солей 2-алкоксикарбонилметилтио-3-алкилбензотиазолия в качестве основного продукта, образуются также 2-алкоксикарбонилметилтиобензотиазол, 2-алкилтиобензотиазол и 2-алкилтио-3-алкоксикарбонилметилбензотиазолий бромид, что указывает на образование сульфониевых солей в качеслий бромид, что указывает на образование сульфониевых солей в качестве промежуточных соединений. Течение реакции исследовалось с помощью ИК-спектроскопии, изотахофореза, а также жидкостной и газовой хроматографии. Обнаружено, что 2-метоксикарбонилметилтио-3-метилбензотиазолий бромид обладает высокой ростостимулирующей активностью ($a_{st} = +7{,}5 \cdot 10^{-11}$ моль дм$^{-3}$).

In the previous works [1—4] it was found that some benzothiazolium salts, prepared by alkylation of benzothiazole or its 2-, 4-, and 6-substituted derivatives, exhibited stimulating and/or inhibiting effects on plant growth.

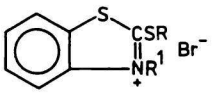
In the present work we have studied alkylations of 3-R^1-2-benzothiazolinethione ($R^1 = CH_3$, C_2H_5, C_3H_7, $CH_2CH=CH_2$, C_4H_9, $CH_2C_6H_5$) with esters of bromoacetic acid in order to prepare 2-RS-3-R^1-benzothiazolium salts. The starting 3-R^1-2-benzothiazolinethiones were prepared from 2-R^1S-benzothiazole by thermic rearrangement of the alkyl group to nitrogen in the presence of iodine [5]. Alkylations were carried out in nitromethane, acetone, dimethylformamide, dimethyl sulfoxide, acetonitrile, and ethanol on allowing the reaction components to stand at room temperature for 24 h or by heating them at the bath temperature of 70—75 °C for 10 h. The highest yields and purity were achieved on 24 h standing in nitromethane (83 %) or on heating in dry acetone (81 %) for 10 h. The yields obtained in other solvents varied in the range of 30—60 %. Characterization of the synthesized compounds is presented in Table 1.

Also alkylations of 2-alkoxycarbonylmethylthiobenzothiazole with methyl iodide, ethyl bromide, and other alkyl halides have been performed, however, pure 2-alkoxycarbonylmethylthio-3-alkylbenzothiazolium salts have not been obtained. This finding is in accordance with the results obtained by *Fry* and *Kendall* [6] who found that in the reaction of 2-alkylthiobenzothiazole with alkyl halide, where the alkyl group was different from that present in the starting compound, a mutual exchange of these groups took place or even elimination of one of these groups occurred giving a mixture of quaternary salts. It is assumed that the exchange of alkyl groups is brought about by formation of an unstable sulfonium salt as the intermediate [7]. Noticeable differences in the yields of the final products, *e.g.* in dimethylformamide (30 %) and nitromethane (83 %) was the reason for studying the alkylation mentioned above in detail. The reaction mixture of 3-methyl-2--benzothiazolinethione and ethyl bromoacetate in dimethylformamide was analyzed by liquid and gas chromatography, isotachophoresis, and IR spectroscopy in order to prove the formation of the possible products *via* the intermediate sulfonium salt according to Scheme 1. The individual components were identified in all cases on the basis of addition of a standard or comparison with a standard (IR). The starting compound *A* was proved by means of gas chromatography. The individual salts could not be determined by this method due to their thermal stability. The compounds *B* and *E* in the reaction mixture were proved by capillary isotachophoresis and liquid chromatography. The compound *B* after isolation from the reaction mixture was shown by liquid chromatography to be contaminated with the compound *E*. The ratio of signal areas (photometric detector, $\lambda = 254$ nm) for the compounds *E* and *B* was $P_E/P_B = 1.45$. The same ratio for the reaction mixture was 1.88 and the ratio of areas representing the compound *E* in the reaction mixture and in the isolated product *B* was $P_E(R)/P_E(A) = 1.3$. It means that in the



Scheme 1

Table 1



Characterization of the synthesized benzothiazolium salts

Compound	R	R¹	Formula	M_r	w_i(calc.)/% w_i(found)/%				Yield	M.p.
					C	H	N	S	%	°C
I	CH_2COOCH_3	CH_3	$C_{11}H_{12}BrNO_2S_2$	334.25	39.52	3.62	4.19	19.18	65	112—114
					39.16	3.60	4.04	18.90		
II	$CH_2COOC_2H_5$	CH_3	$C_{12}H_{14}BrNO_2S_2$	348.30	41.38	4.05	4.02	18.41	83	123—124
					41.39	4.07	4.12	18.40		
III	$CH_2COOC_3H_7$	CH_3	$C_{13}H_{16}BrNO_2S_2$	362.32	43.09	4.45	3.87	17.69	77	91—92
					42.93	4.78	3.78	17.60		
IV	$CH_2COOC_3H_7$-i	CH_3	$C_{13}H_{16}BrNO_2S_2$	362.32	43.09	4.45	3.87	17.69	74	113—115
					42.83	4.31	3.83	17.42		
V	$CH_2COOCH_2CH=CH_2$	CH_3	$C_{13}H_{14}BrNO_2S_2$	360.31	43.34	3.92	3.89	17.79	86	97—99
					43.32	3.91	3.88	17.78		
VI	CH_2COOCH_3	C_2H_5	$C_{12}H_{14}BrNO_2S_2$	348.29	41.38	4.05	4.02	18.41	26	112—114
					41.71	4.08	4.08	18.03		
VII	$CH_2COOC_2H_5$	C_2H_5	$C_{13}H_{16}BrNO_2S_2$	362.32	43.09	4.45	3.87	17.70	56	99—100
					42.96	4.38	3.93	17.80		
VIII	$CH_2COOC_3H_7$	C_2H_5	$C_{14}H_{18}BrNO_2S_2$	376.34	44.68	4.82	3.72	17.04	46	92—95
					44.34	4.98	3.68	17.06		
IX	$CH_2COOC_3H_7$-i	C_2H_5	$C_{14}H_{18}BrNO_2S_2$	376.34	44.68	4.82	3.72	17.04	46	117—118
					44.54	4.78	3.86	16.94		
X	$CH_2COOCH_2CH=CH_2$	C_2H_5	$C_{14}H_{16}BrNO_2S_2$	374.33	44.92	4.31	3.74	17.13	47	72—74
					44.81	4.18	3.61	17.12		
XI	CH_2COOCH_3	C_3H_7	$C_{13}H_{16}BrNO_2S_2$	362.31	43.09	4.45	3.87	17.70	37	102—103
					43.28	4.49	3.88	17.63		

Table 1 (Continued)

Compound	R	R^1	Formula	M_r	w_i(calc.)/% w_i(found)/%				Yield	M.p.
					C	H	N	S	%	°C
XII	$CH_2COOC_2H_5$	C_3H_7	$C_{14}H_{18}BrNO_2S_2$	376.33	44.68	4.82	3.72	17.04	40	104—106
					44.58	4.71	3.78	17.09		
XIII	$CH_2COOC_3H_7$	C_3H_7	$C_{15}H_{20}BrNO_2S_2$	390.36	46.15	5.16	3.59	16.43	30	99—100
					46.21	5.18	3.65	16.58		
XIV	$CH_2COOC_3H_7$-i	C_3H_7	$C_{15}H_{20}BrNO_2S_2$	390.36	46.15	5.16	3.59	16.43	76	128—130
					45.99	5.13	3.71	16.43		
XV	$CH_2COOCH_2CH=CH_2$	C_3H_7	$C_{15}H_{18}BrNO_2S_2$	388.35	46.39	4.67	3.61	16.51	21	81—83
					46.42	4.58	3.67	16.44		
XVI	CH_2COOCH_3	$CH_2CH=CH_2$	$C_{13}H_{14}BrNO_2S_2$	360.31	43.34	3.92	3.89	17.79	65	103—106
					43.23	3.82	3.98	17.66		
XVII	$CH_2COOC_2H_5$	$CH_2CH=CH_2$	$C_{14}H_{16}BrNO_2S_2$	374.33	44.92	4.31	3.74	17.13	32	110—115
					45.18	4.24	3.90	17.50		
XVIII	CH_2COOCH_3	C_4H_9	$C_{14}H_{18}BrNO_2S_2$	376.34	44.68	4.82	3.72	17.04	53	91—92
					44.42	4.81	3.79	16.96		
XIX	$CH_2COOC_2H_5$	C_4H_9	$C_{15}H_{20}BrNO_2S_2$	390.37	46.15	5.16	3.59	16.43	16	87—88
					45.90	5.20	3.58	16.20		
XX	$CH_2COOC_3H_7$	C_4H_9	$C_{16}H_{22}BrNO_2S_2$	404.39	47.52	5.48	3.46	15.86	35	100—101
					47.39	5.37	3.67	15.63		
XXI	$CH_2COOCH_2CH=CH_2$	C_4H_9	$C_{16}H_{20}BrNO_2S_2$	402.38	47.76	5.01	3.48	15.94	35	89—90
					47.66	5.04	3.61	15.85		
XXII	CH_2COOCH_3	$CH_2C_6H_5$	$C_{17}H_{16}BrNO_2S_2$	410.34	49.76	3.93	3.41	15.63	17	193—195
					49.32	3.78	3.43	15.49		
XXIII	$CH_2COOC_2H_5$	$CH_2C_6H_5$	$C_{18}H_{18}BrNO_2S_2$	424.37	50.94	4.28	3.30	15.11	7	195—197
					51.02	4.32	3.27	15.03		

reaction mixture was 1.3 times more compound *E*. By capillary isotachophoresis the presence of the compound *E* was not proved in the isolated product *B*. Low reproducibility of the zone *E* was attributed to thermal instability of the compound and will be the subject of a separate study. We assume that due to isotachophoretic driving current generating heat the compound *E* decomposes more rapidly than at room temperature. The compound *G* was not confirmed by either of the identification methods. It can be explained by the fact that it is less stable than the compound *E* and is formed probably in small amounts during the reaction. Direct preparation from 3-ethoxycarbonylmethyl-2-benzothiazolinethione by treatment with ethyl bromoacetate was unsuccessful, too. The individual compounds were concentrated by preparative isotachophoresis and liquid chromatography and used for their identification by IR spectroscopy. The presence of the compounds *E*, *B*, and *D* in the reaction mixture was confirmed by this method. The wavenumbers of stretching vibrations with the individual compounds were identical with that of the standard: $\tilde{\nu}/\mathrm{cm}^{-1}$: *E* – ν(C=O) 1730, ν(C=C) 1580, δ_s(CH) 1400, δ_{as}(CH) 1447, ν(C—O—C) 1300—1350; *B* – ν(C=O) 1720, ν(C=C) 1570, δ_s(CH) 1425, δ_{as}(CH) 1375, 1410, 1452, ν(C—O—C) 1250—1297; *D* – ν(CH) 3040, ν(CH_3) 2900, δ_s(CH) 1410, δ_{as}(CH) 1445.

The formation of the expected compound *F* was not proved. Its occurrence is limited by preferential formation of the compound *E* (higher concentration of $BrCH_2COOC_2H_5$ by 0.005 mol dm^{-3} in the reaction medium) and by the fact that CH_3Br (b.p. = 4.6 °C) may leak out from the reaction mixture during synthesis. The analogous mixture in nitromethane was analyzed in the same way. Gas chromatography and ^{1}H NMR spectroscopy revealed only the presence of the compounds *A* and *B*. This finding was in accordance with the stability of the compound *B* in dimethylformamide and nitromethane established by UV and ^{1}H NMR spectroscopy. While in dimethylformamide the compound *B* is in equilibrium with the compound *C*, in nitromethane the compound *C* was not proved. This points to high stability of *B* in this reaction medium. It means that due to polarity and solvation effect of dimethylformamide *B* may decompose to *C* and that enables the formation of the intermediate sulfonium salt. Of the investigated solvents, nitromethane as less polar solvent was shown to be the most suitable reaction medium for the studied synthesis at room temperature. The structures of 2-alkoxycarbonylmethylthio-3-alkylbenzothiazolium salts were proved by evaluation of ^{1}H NMR spectra which showed multiplets of aromatic hydrogens of the benzothiazole heterocycle at $\delta = 7.9$ ppm to 7.2 ppm. The spectra of the compounds with methyl group attached to nitrogen atom exhibited significant signals at $\delta = 3.8$ ppm. The signals observed in the spectra of the compounds having other alkyls on the heterocyclic nitrogen are presented in Table 2. The spectra revealed also singlets of SCH_2COOR groups at $\delta = 4.2$ ppm.

Table 2

^{1}H NMR chemical shifts (δ/ppm) of the synthesized 2-alkoxycarbonylmethylthio--3-alkylbenzothiazolium salts

Compound	
I	7.9—7.2 (ar, 4H, m); 4.19 (S—CH_2, 2H, s); 3.88 ($\overset{+}{N}$—CH_3, 3H, s); 3.68 (O—CH_3, 3H, s)
II	7.9—7.2 (ar, 4H, m); 4.16 (S—CH_2, 2H, s); 4.01 (O—CH_2, 2H, q); 3.87 ($\overset{+}{N}$—CH_3, 3H, s); 0.95 (CH_3, 3H, t)
III	7.9—7.2 (ar, 4H, m); 4.18 (S—CH_2, 2H, s); 3.93 (O—CH_2, 2H, t); 3.87 ($\overset{+}{N}$—CH_3, 3H, s); 1.36 (CH_2, 2H, sx); 0.65 (CH_3, 3H, t)
IV	7.9—7.2 (ar, 4H, m); 4.85 (CH, 1H, h); 4.13 (S—CH_2, 2H, s); 3.86 ($\overset{+}{N}$—CH_3, 3H, s); 0.96 (CH_3, 6H, d)
V	7.9—7.2 (ar, 4H, m); 5.5 (=CH, 1H, m); 5.0 (=CH_2, 2H, m); 4.43 (O—CH_2, 2H, d); 4.20 (S—CH_2, 2H, s); 3.88 ($\overset{+}{N}$—CH_3, 3H, s)
VI	7.9—7.2 (ar, 4H, m); 4.38 ($\overset{+}{N}$—CH_2, 2H, q); 4.20 (S—CH_2, 2H, s); 3.56 (O—CH_3, 3H, s); 1.25 (CH_3, 3H, t)
VII	7.9—7.2 (ar, 4H, m); 4.38 ($\overset{+}{N}$—CH_2, 2H, q); 4.21 (S—CH_2, 2H, s); 4.03 (O—CH_2, 2H, q); 1.25 (CH_3, 3H, t); 0.98 (CH_3, 3H, t)
VIII	7.9—7.2 (ar, 4H, m); 4.40 ($\overset{+}{N}$—CH_2, 2H, q); 4.24 (S—CH_2, 2H, s); 3.94 (O—CH_2, 2H, t); 1.38 (CH_2, 2H, sx); 1.25 (CH_3, 3H, t); 0.63 (CH_3, 3H, t)
IX	7.9—7.2 (ar, 4H, m); 4.81 (CH, 1H, h); 4.38 ($\overset{+}{N}$—CH_2, 2H, q); 4.15 (S—CH_2, 2H, s); 1.23 (CH_3, 3H, t); 0.98 (CH_3, 6H, d)
X	7.9—7.2 (ar, 4H, m); 5.5 (=CH, 1H, m); 5.0 (=CH_2, 2H, m); 4.4 ($\overset{+}{N}$—CH_2, O—CH_2, 4H, m); 4.23 (S—CH_2, 2H, s); 1.25 (CH_3, 3H, t)
XI	7.9—7.2 (ar, 4H, m); 4.28 ($\overset{+}{N}$—CH_2, 2H, t); 4.20 (S—CH_2, 2H, s); 3.59 (O—CH_3, 3H, s); 1.70 (CH_2, 2H, sx); 0.73 (CH_3, 3H, t)
XII	7.9—7.2 (ar, 4H, m); 4.29 ($\overset{+}{N}$—CH_2, 2H, t); 4.20 (S—CH_2, 2H, s); 4.02 (O—CH_2, 2H, q); 1.70 (CH_2, 2H, sx); 0.95 (CH_3, 3H, t); 0.73 (CH_3, 3H, t)
XIII	7.9—7.2 (ar, 4H, m); 4.29 ($\overset{+}{N}$—CH_2, 2H, t); 4.20 (S—CH_2, 2H, s); 3.93 (O—CH_2, 2H, t); 1.70 (CH_2, 2H, sx); 1.36 (CH_2, 2H, sx); 0.70 (CH_3, 6H, t)
XIV	7.9—7.2 (ar, 4H, m); 4.85 (CH, 1H, h); 4.28 ($\overset{+}{N}$—CH_2, 2H, t); 4.16 (S—CH_2, 2H, s); 1.69 (CH_2, 2H, sx); 0.94 (CH_3, 6H, d); 0.70 (CH_3, 3H, t)
XV	7.9—7.2 (ar, 4H, m); 5.5 (=CH, 1H, m); 5.0 (=CH_2, 2H, m); 4.43 (O—CH_2, 2H, d); 4.30 ($\overset{+}{N}$—CH_2, 2H, t); 4.23 (S—CH_2, 2H, s); 1.70 (CH_2, 2H, sx); 0.73 (CH_3, 3H, t)

Table 2 (Continued)

Compound	
XVI	7.9—7.2 (ar, 4H, m); 5.5 (=CH, 1H, m); 5.0 ($\overset{+}{N}$—CH_2, $=CH_2$, 4H, m); 4.20 (S—CH_2, 2H, s); 3.56 (O—CH_3, 3H, s)
XVIII	7.9—7.2 (ar, 4H, m); 4.33 ($\overset{+}{N}$—CH_2, 2H, t); 4.20 (S—CH_2, 2H, s); 3.56 (O—CH_3, 3H, s); 1.7 (CH_2, 2H, m); 1.2 (CH_2, 2H, m); 0.63 (CH_3, 3H, t)
XIX	7.9—7.2 (ar, 4H, m); 4.31 ($\overset{+}{N}$—CH_2, 2H, t); 4.19 (S—CH_2, 2H, s); 4.02 (O—CH_2, 2H, q); 1.6 (CH_2, 2H, m); 1.3—0.5 (CH_2, CH_3, 5H, m)
XX	7.9—7.2 (ar, 4H, m); 4.35 ($\overset{+}{N}$—CH_2, 2H, t); 4.26 (S—CH_2, 2H, s); 3.94 (O—CH_2, 2H, t); 1.8—1.0 (CH_2, 6H, m); 0.63 (CH_3, 6H, t)
XXI	7.9—7.2 (ar, 4H, m); 5.5 (=CH, 1H, m); 5.0 ($=CH_2$, 2H, m); 4.43 (O—CH_2, 2H, d); 4.33 ($\overset{+}{N}$—CH_2, 2H, t); 4.24 (S—CH_2, 2H, s); 1.6 (CH_2, 2H, m); 1.1 (CH_2, 2H, m); 0.63 (CH_3, 3H, t)
XXII	7.2—7.9 (m, 4H, ar); 5.52 ($\overset{+}{N}$—CH_2, 2H, t); 4.25 (S—CH_2, 2H, s)
XXIII	7.2—7.9 (ar, 4H, m); 5.52 ($\overset{+}{N}$—CH_2, 2H, t); 4.25 (S—CH_2, 2H, s)

The synthesized compounds were tested on seeds of *Vicia sativa* for growth--regulating effect on the root system. The results obtained (Table 3) allow to conclude that a new group of compounds with plant growth-regulating properties was discovered. The activity of some of the synthesized derivatives was equal to or even higher than those of the used standards, *e.g.* the stimulating activity of *I*, *IV*, *XIV* and the inhibiting activity of *III*, *V*, *VIII*, *X*, *XVII*, *XVIII*, and *XX*. For practical utilization it is important that their synthesis is simple and majority of these compounds are well soluble in water. In spite of low number of compounds, the significant results enable to make some preliminary contemplations about the relations of structures and activities. When retaining the methyl ester group in the position 2 and changing the alkyl in the position 3 from methyl to butyl (compounds *I*, *VI*, *XI*, *XVI*, and *XVIII*), the stimulating activity decreased with lengthening of the aliphatic chain and with *XVI* turned to inhibiting activity. When retaining the methyl group in the position 3 and increasing the number of carbons in the ester group (compounds *I*, *II*, *III*, and *V*) a continuous change from high stimulating activity ($a_{st} = +7.15 \times 10^{-11}$ mol dm^{-3}) to high inhibiting activity ($a_{in} = -5.15 \times 10^{-13}$ mol dm^{-3}) was observed. These results are in accordance with the previous observations [1—4], *i.e.* that the effect of the methyl group in different combinations is, in the average, most intensively reflected in the biological activity. When retaining the ethyl ester group and changing the 3-alkyl group a fast change from stimulating activity (*I*) to inhibiting activity was observed which rapidly

Table 3

Growth-regulating activity of benzothiazolium salts on *Vicia sativa*

Compound	Stimulation		Inhibition		Compound	Stimulation		Inhibition	
	d_{st}	a_{st}	$-d_{in}$	a_{in}		d_{st}	a_{st}	$-d_{in}$	a_{in}
	mm	mol dm^{-3}	mm	mol dm^{-3}		mm	mol dm^{-3}	mm	mol dm^{-3}
I	7.15	10^{-11}			*XIV*	3.80	10^{-11}		
II	4.05	10^{-7}			*XV*	1.20	10^{-13}		
III			3.55	10^{-13}	*XVI*			13.40	10^{-3}
IV	5.50	10^{-9}			*XVII*			12.10	10^{-3}
V			5.15	10^{-13}	*XVIII*			6.45	10^{-13}
VI	3.85	10^{-7}			*XIX*	3.10	10^{-7}		
VII			4.90	10^{-13}	*XX*			23.70	10^{-3}
VIII			21.60	10^{-}	*XXI*	1.25	10^{-}	1.65	10^{-13}
IX	2.00	10^{-5}	1.50	10^{-13}	*XXII*	4.10	10^{-7}		
X			4.30	10^{-13}	*XXIII*			6.00	10^{-}
XI	2.95	10^{-11}	9.80	10^{-3}	IAA	3.10	10^{-12}	18.55	10^{-}
XII	1.55	10^{-7}			2,4-D	4.95	10^{-}	23.30	10^{-}
XIII	2.55	10^{-}			CCC			3.85	10^{-}

IAA — β-indolylacetic acid; 2,4-D — 2,4-dichlorophenoxyacetic acid; CCC — 2-chloroethyltrimethylammonium chloride.

decreased and the 3-butyl derivative (*XIX*) showed a stimulating activity. In the case of allyl esters (*V*, *X*, *XV*, and *XXI*), a very fast decrease from high inhibiting activity (3-methyl derivative) to stimulating activity (*N*-propyl derivative (*XV*)) was observed. Such a trend was valid also for the propyl ester group. These relationships are studied in recognition of the fact that they are not conditioned only by one factor.

We have accomplished antibacterial tests on *Staphylococcus aureus Mau 29/58, Staphylococcus aureus Mau 2/560, Bacillus subtilis 18/66, Escherichia coli 326/71,* and on yeasts *Candida pseudotropicalis.* The compounds were effective in minimal inhibition concentration from 50—400 μg/disc. The results of tests for herbicidal activity were negative.

Experimental

3-Alkyl-2-benzothiazolinethiones were synthesized from 2-alkylthiobenzothiazoles [5]. Melting points were established on a Kofler block. Characterization of the synthesized compounds is presented in Table 1. ^{1}H NMR spectra, presented in Table 2, were measured in deuterated trifluoroacetic acid with a Tesla 487 apparatus at 80 MHz using hexamethyldisiloxane as internal standard. IR spectra were recorded with a Perkin—Elmer 180 spectrophotometer in Nujol suspension. Isotachophoresis was measured with an Isotachophoretic Analyzer VÚZPJT, Spišská Nová Ves. The solution of 10^{-2} M-($CH_3COOK + CH_3COOH$) (pH = 5.6) was used as the leading electrolyte and the solution of 5×10^{-3} M-β-alanine as the terminating electrolyte. The driving current was 200 μA (first step) and 40 μA (second step), conductometric detection. Liquid chromatography: pump HPP 4001 (Laboratórní přístroje, Prague), Knauer cyclic feeder (West Berlin), cycle volume 38 mm^3, LCD 254 detector (Laboratórní přístroje, Prague). A stainless-steel column (6 mm × 250 mm) of Separon C_{18} 10 μm was used in preparative experiments and a stainless-steel column (6 mm × 100 mm) of Separon C_{18} 7 μm was used for analytical purposes. Gas chromatography was provided with a Chrom 4 apparatus on a column (150 cm × 0.3 cm) of 3 % Carbowax 20 M + 4 % KOH on Chromosorb W using nitrogen as the carrier gas; inlet pressure 0.04 MPa, column temperature 150—200 °C. Growth stimulation of roots was established according to [8]. The standard 3-ethoxycarbonylmethyl-2-methylthiobenzothiazolium iodide was prepared according to [9].

2-Alkoxycarbonylmethylthio-3-alkylbenzothiazolium salts

3-Alkyl-2-benzothiazolinethione (alkyl = CH_3, C_2H_5, C_3H_7, $CH_2CH=CH_2$, C_4H_9, $CH_2C_6H_5$) (0.02 mol) was dissolved in nitromethane (8 cm^3) and alkyl bromoacetate (alkyl = CH_3, C_2H_5, C_3H_7, C_3H_7-i, $CH_2CH=CH_2$) (0.025 mol) was added. The reaction mixture was allowed to stand at room temperature for 24 h. The precipitated quaternary salt was washed with dry acetone. In case of the compounds *XXII* and *XXIII* the reaction mixture was heated at the bath temperature 80—85 °C for 24 h.

References

1. Sutoris, V., Halgaš, J., Sekerka, V., Foltínová, P., and Gáplovský, A., *Chem. Zvesti 37*, 653 (1983).
2. Halgaš, J., Sutoris, V., Sekerka, V., Foltínová, P., and Sólčániová, E., *Chem. Zvesti 37*, 663 (1983).
3. Halgaš, J., Sutoris, V., Foltínová, P., and Sekerka, V., *Chem. Zvesti 37*, 799 (1983).
4. Sutoris, V., Halgaš, J., Foltínová, P., and Sekerka, V., *Chem. Zvesti 38*, 247 (1984).
5. Sexton, W. A., *J. Chem. Soc. 1939*, 470.
6. Fry, D. J. and Kendall, J. D., *J. Chem. Soc. 1951*, 1716.
7. Moore, C. G. and Wight, E. S., *J. Chem. Soc. 1952*, 4237.
8. Sutoris, V., Sekerka, V., and Halgaš, J., *Czechoslov. Appl.* 7634-80.
9. Sutoris, V., Gáplovský, A., and Sekerka, V., *Chem. Papers*, in press.

Translated by A. Kardošová