Benzothiazole compounds
XXVIII. Synthesis of 2-styrylbenzothiazolium salts substituted at position 3 and their biological activity

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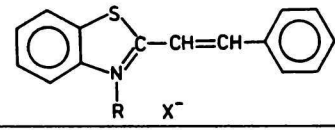
2-Styrylbenzothiazolium salts substituted at the position 3 were prepared by alkylation of 2-styrylbenzothiazole with methyl iodide, dimethyl sulfate, allyl bromide, propargyl bromide, benzyl bromide, bromoacetic acid, and bromoacetic acid esters. Their structure was proved by UV, IR, and ^{1}H NMR spectra. The compounds showed the activity as plant-growth regulators, and affected both the cells division of *Euglena gracilis* and the synthesis of chlorophyll. The antibacterial and antifungal activities were also found.

Соли 2-стирилбензотиазолия, замещенные в положении 3, были получены посредством алкилирования 2-стирилбензотиазола иодистым метилом, диметилсульфатом, бромистым аллилом, бромистым пропаргилом, бромистым бензилом, бромуксусной кислотой и эфирами бромуксусной кислоты. Их строение было доказано с помощью УФ, ИК и ^{1}H ЯМР спектрометрии. Полученные соединения обладали свойством регулировать рост растений и влияли как на деление клеток *Euglena gracilis*, так и на синтез хлорофилла. Кроме того были обнаружены бактерицидная и фунгицидная активности этих соединений.

Just a little attention has been paid to the synthesis of 2-styrylbenzothiazolium salts substituted at the position 3. So far, only 2-styryl-3-methylbenzothiazolium methyl sulfate (*I*), iodide (*II*), and perchlorate (*III*) have been described. The compounds *II* and *III* were prepared by an anion-exchange reaction from *I* [1].

Table 1

Characterization of the synthesized benzothiazolium salts



Compound	R	X	Formula	M_r	w_i(calc.)/% / w_i(found)/%				Yield	M.p.
					C	H	N	S	%	°C
I	CH_3	CH_3SO_4	$C_{17}H_{15}NO_4S_2$	363.46	56.18	4.16	3.85	17.64	65	186—189
					55.89	4.09	4.15	17.63		
II	CH_3	I	$C_{16}H_{14}INS$	379.25	50.39	3.67	3.67	8.39	50	245—247
					50.36	3.62	3.67	8.38		
III	CH_3	ClO_4	$C_{16}H_{14}ClNO_4S$	353.81	54.31	3.99	3.91	9.04	80	250—253
					54.20	3.82	4.07	9.11		
IV	CH_3	BF_4	$C_{16}H_{14}BF_4NS$	339.35	56.63	4.16	4.13	9.45	90	239—241
					56.89	4.21	4.17	9.55		
V	$CH_2C_6H_5$	Br	$C_{22}H_{18}BrNS$	408.35	64.71	4.44	3.43	7.85	45	236—239
					64.92	4.31	3.28	8.05		
VI	$CH_2C_6H_5$	ClO_4	$C_{22}H_{18}ClNO_4S$	427.89	61.75	4.24	3.27	7.49	80	241—243
					61.62	4.31	3.18	7.57		
VII	$CH_2C_6H_5$	BF_4	$C_{22}H_{18}BF_4NS$	427.90	63.60	4.37	3.37	7.72	90	240—242
					63.82	4.21	3.34	7.71		

Table 1 (Continued)

Compound	R	X	Formula	M_r	w_i(calc.)/% w_i(found)/%				Yield	M.p.
					C	H	N	S	%	°C
VIII	$CH_2C_6H_5$	NO_3	$C_{22}H_{18}N_2O_3S$	390.46	67.67 67.40	4.64 4.56	7.17 7.10	8.21 8.24	83	219—220
IX	$CH_2CH=CH_2$	Br	$C_{18}H_{16}BrNS$	358.29	60.34 59.98	4.45 4.20	3.91 3.84	8.92 8.74	45	223—225
X	$CH_2C\equiv CH$	Br	$C_{18}H_{14}BrNS$	356.28	60.68 60.92	3.96 3.80	3.93 4.05	9.00 8.82	22	226—229
XI	CH_2COOH	Br	$C_{17}H_{14}BrNO_2S$	376.27	54.27 54.30	3.75 3.60	3.72 3.57	8.52 8.27	20	230—233
XII	$CH_2CO_2CH_3$	Br	$C_{18}H_{16}BrNO_2S$	390.30	55.39 55.10	4.13 4.11	3.59 3.58	8.21 8.32	37	195—197
XIII	$CH_2CO_2C_2H_5$	Br	$C_{19}H_{18}BrNO_2S$	404.32	56.44 56.28	4.48 4.38	3.46 3.58	7.93 7.73	36	216—219
XIV	$CH_2CO_2C_3H_7$-i	Br	$C_{20}H_{20}BrNO_2S$	418.36	57.42 57.23	4.82 4.81	3.35 3.21	7.66 7.72	42	214—217
XV	$CH_2CO_2C_3H_7$	Br	$C_{20}H_{20}BrNO_2S$	418.36	57.42 57.08	4.82 4.66	3.35 3.34	7.66 7.61	45	203—206

Table 1 (Continued)

Compound	R	X	Formula	M_r	w_i(calc.)/% w_i(found)/%				Yield	M.p.
					C	H	N	S	%	°C
XVI	$CH_2CO_2CH=CH_2$	Br	$C_{19}H_{16}BrNO_2S$	402.32	56.72 56.53	4.01 4.02	3.48 3.46	7.97 7.93	40	207–210
XVII	$CH_2CO_2CH_2CH=CH_2$	Br	$C_{20}H_{18}BrNO_2S$	416.34	57.70 57.57	4.36 4.25	3.37 3.39	7.70 7.53	39	209—212
XVIII	$CH_2CO_2C_4H_9$	Br	$C_{21}H_{22}BrNO_2S$	432.38	58.38 58.07	5.60 5.49	3.24 3.30	7.41 7.46	43	187—189
XIX	$CH_2CO_2C_5H_{11}$	Br	$C_{22}H_{24}BrNO_2S$	442.38	59.78 59.91	5.47 5.34	3.16 3.31	7.23 7.15	41	176—179
XX	$CH_2CO_2C_7H_{15}$	Br	$C_{24}H_{28}BrNO_2S$	474.46	60.76 60.45	5.95 5.91	2.95 2.91	6.76 6.93	30	174—177
XXI	$CH_2CO_2CH_2C_6H_5$	Br	$C_{24}H_{20}BrNO_2S$	466.38	61.82 61.55	4.32 4.16	3.00 3.01	6.87 7.04	32	192—196

Table 2

^{1}H NMR, UV, and IR spectral data of the synthesized compounds

Compound	δ/ppm	λ_{max}/nm	$\frac{\varepsilon_1 . 10^{-3}}{dm^2\ mol}$	$\frac{\nu(C=O)}{\tilde{\nu}/cm^{-1}}$	$\frac{\nu(C=C)}{\tilde{\nu}/cm^{-1}}$
I	7.35—8.50 (m, 11H, Ar, —CH=CH—), 4.34 (s, 3H, $\overset{+}{N}$—CH_3)[a]	337	22.66		1603
II	7.40—8.50 (m, 11H, Ar, —CH=CH—), 4.35 (s, 3H, $\overset{+}{N}$—CH_3)[a]	372	41.08		1603
III	7.40—8.50 (m, 11H, Ar, —CH=CH—), 4.38 (s, 3H, $\overset{+}{N}$—CH_3)[a]	372	28.67		1604
IV	6.80—7.80 (m, 10H, Ar, —CH=CH—), 3.96 (s, 3H, $\overset{+}{N}$—CH_3)[a]	372	28.28		1603
V	6.70—7.90 (m, 16H, Ar, —CH=CH—), 5.69 (s, 2H, $\overset{+}{N}$—CH_2—)[b]	378	35.71		1603
VI	6.70—7.90 (m, 16H, Ar, —CH=CH—), 5.67 (s, 2H, $\overset{+}{N}$—CH_2—)[b]	378	37.88		1602
VII	6.70—7.90 (m, 16H, Ar, —CH=CH—), 5.64 (s, 2H, $\overset{+}{N}$—CH_2—)[b]	378	33.92		1604
VIII	7.00—8.00 (m, 16H, Ar, —CH=CH—), 5.60 (s, 2H, $\overset{+}{N}$—CH_2—)[b]	373	41.67		1603
IX	7.30—8.60 (m, 11H, Ar, —CH=CH—), 5.00—6.50 (m, 5H, $\overset{+}{N}$—CH_2—$CH=CH_2$)[a]	375	30.47		1601
X	7.05—8.62 (m, 11H, Ar, —CH=CH—), 6.01 (s, 2H, $\overset{+}{N}$—CH_2—), 3.70 (s, 1H, ≡CH)[a]	358	26.43		1630
XI	7.35—8.60 (m, 11H, Ar, —CH=CH—), 5.99 (s, 2H, $\overset{+}{N}$—CH_2—)[a]	374	23.55	1758	1612
XII	7.40—8.60 (m, 11H, Ar, —CH=CH—), 6.09 (s, 2H, $\overset{+}{N}$—CH_2—), 3.78 (s, 3H, —OCH_3)[a]	378	36.02	1760	1614
XIII	7.40—8.50 (m, 11H, Ar, —CH=CH—), 6.07 (s, 2H, $\overset{+}{N}$—CH_2—), 4.20 (q, 2H, —OCH_2), 1.20 (t, 3H, —CH_3)[a]	378	36.80	1748	1610
XIV	6.80—7.90 (m, 11H, Ar, —CH=CH—), 5.41 (s, 2H, $\overset{+}{N}$—CH_2—), 4.80 (m, 1H, —OCH), 0.87 (d, 6H, $(CH_3)_2$)[b]	382	29.72	1741	1611

Table 2 (Continued)

Compound	δ/ppm	λ_{max}/nm	$\varepsilon_1 . 10^{-3}$ / dm² mol	ν(C=O) / $\tilde{\nu}$/cm^{-1}	ν(C=C) / $\tilde{\nu}$/cm^{-1}
XV	6.80—7.90 (m, 11H, Ar, —CH=CH—), 5.45 (s, 2H, $\overset{+}{N}$—CH_2—), 3.90 (t, 2H, —OCH_2), 1.26 (m, 2H, —CH_2—), 0.50 (t, 3H, —CH_3)[b]	378	33.18	1748	1611
XVI	6.60—8.10 (m, 12H, Ar, —CH=CH—, —OCH=), 5.51 (s, 2H, $\overset{+}{N}$—CH_2—), 4.71 (dd, 1H, =CH_2 *trans*), 4.40 (dd, 1H, =CH_2 *cis*)[b]	380	28.20	1764	1610
XVII	7.00—7.90 (m, 11H, Ar, —CH=CH—), 5.46 (s, 2H, $\overset{+}{N}$—CH_2—), 4.70—5.50 (m, 3H, —CH=CH_2), 4.40 (d, 2H, —OCH_2—)[b]	378	28.61	1750	1607
XVIII	6.90—7.90 (m, 11H, Ar, —CH=CH_2—), 5.43 (s, 2H, $\overset{+}{N}$—CH_2—), 3.92 (t, 2H, —OCH_2—), 0.50—1.30 (m, 7H, —CH_2—, CH_3)[b]	382	29.58	1745	1609
XIX	6.90—7.90 (m, 11H, Ar, —CH=CH—), 5.41 (s, 2H, $\overset{+}{N}$—CH_2—), 3.90 (t, 2H, —OCH_2—), 0.50—1.30 (m, 9H, —CH_2—, —CH_3)[b]	381	27.45	1745	1609
XX	6.80—8.00 (m, 11H, Ar, —CH=CH—), 5.46 (s, 2H, $\overset{+}{N}$—CH_2—), 3.92 (t, 2H, —OCH_2—), 0.60—1.50 (m, 13H, —CH_2—, —CH_3)[b]	382	35.55	1752	1611
XXI	6.70—7.90 (m, 16H, Ar, —CH=CH—), 5.41 (s, 2H, $\overset{+}{N}$—CH_2—), 1.91 (s, 2H, —OCH_2—)[b]	375	23.03	1747	1610

a) In DMSO-d_6; *b*) In CF_3COOD.

The present paper is linked up with our previous results on benzothiazolium salts research [2]. Our intention was to carry out various alkylations of 2-styrylbenzothiazole and thus to prepare 2-styryl-3-R-benzothiazolium salts, to characterize them by spectral methods and to examine their activity as plant-growth regulators, in cells division and synthesis of chlorophyll of *Euglena gracilis* as well as in antibacterial and antifungal areas. Concerning the activity tests, we expected the influence of both the character of a substituent at the position 3 (especially the nature of an ester group) and the character of a counterion.

2-Styrylbenzothiazole was prepared in 95 % yield by condensation of 2-methylbenzothiazole with benzaldehyde according to *Dryanská*'s procedure [3]. Its alkylation with alkyl halides, bromoacetic acid esters, and dimethyl sulfate led to 2-styryl-3-R-benzothiazolium salts listed in Table 1. Reactions with methyl iodide and dimethyl sulfate were performed in dry acetone at reflux temperature. The rest of alkylations was carried out in dry acetonitrile at 70—80 °C (bath temperature). A higher temperature caused formation of black, not identified oily material. In order to learn more deeply the role of an anion in biological activity, the anions of 2-styrylbenzothiazolium bromide and iodide were replaced by ClO_4^-, BF_4^-, NO_3^-, and $CH_3SO_4^-$. The synthesized derivatives of benzothiazolium salts exhibit the characteristic absorption in UV region between 372 nm and 382 nm (Table 2). The exceptions are compounds *I* and *X* with λ_{max} at considerably lower wavelengths. In case of the derivative *I* a plausible explanation lies in a different polarizability (and the solvation related to it) of the anion $CH_3SO_4^-$. Electron-donating effect of the propargyl group is responsible for the observed trend in case of the derivative *X*. The dependence of wavenumbers of bands belonging to ν(C=O) vibrations on the alkoxy group (compounds *XI*—*XXI*) follows almost exactly the same pattern described for the chloroacetic acid esters [4], however, the dependence on the inductive effect is not linear. The wavenumbers of ν(C=C) vibration bands do not change significantly their positions either, when the R is changed, except for the derivative *X*. The position of ν(C=C) vibration at a much higher wavenumber than in the rest of derivatives is a consequence of a large inductive effect of the propargyl group ($\sigma^* = 0.76$) [5]. The influence of a counterion on the position of this band is negligible. In UV spectra taken in protic and aprotic solvents (H_2O, CH_3CN) a remarkable change of molar absorption coefficients occurs. In ^{1}H NMR spectra recorded at various concentrations of our salts ($c = 10^{-1}$—10^{-3} mol dm^{-3}) one can observe that chemical shift of alkyl groups protons is concentration-dependent; *e.g.* the chemical shift of methylene protons —$\overset{+}{N}$—CH_2— in 2-styryl-3-ethoxycarbonylmethylbenzothiazolium bromide (*XIII*) ranges from $f =$ = 505—502 Hz depending on the concentration. This fact points to the capabil-

Table 3

Effect of the synthesized compounds on *Euglena gracilis*

Compound	Cells % / Mutants % / Chlorophyll %							
	400	200	100	50	10	5	1	0.1
				ϱ/(μg cm^{-3})				
I	0/0/0	0/0/0	0/0/0	2/6/8	13/2/26	18/0/38	65/0/73	99/0/86
II	0/0/0	0/0/0	0/0/0	2/0/13	16/0/26	23/0/54	68/0/80	100/0/99
III	0/0/0	0/0/0	0/0/0	3/0/13	17/0/28	23/0/56	65/0/82	99/0/98
IV	0/0/0	0/0/0	0/0/0	0/0/0	6/0/7	23/0/36	68/0/70	98/0/89
V	0/0/0	0/0/0	0/0/0	3/0/15	42/0/36	52/0/48	76/0/70	99/0/97
VI	0/0/0	0/0/0	0/0/0	7/0/16	38/0/40	54/0/55	74/0/72	95/0/99
VII	0/0/0	0/0/0	0/0/0	2/0/8	24/0/26	35/0/40	75/0/69	97/0/95
VIII	0/0/0	0/0/0	0/0/0	10/5/26	35/2/65	56/0/78	76/0/83	95/0/96
IX	0/0/0	0/0/0	0/0/0	0/0/0	24/2/36	63/0/48	70/0/70	90/0/86
X	0/0/0	0/0/0	0/0/0	0/0/0	3/0/13	26/0/30	56/0/70	88/0/83
XI	3/0/63	32/0/68	69/0/70	86/0/85	89/0/90	99/0/96	100/0/100	100/0/100
XII	0/0/0	0/0/0	16/0/48	50/0/70	68/0/79	86/0/90	98/0/100	102/0/101
XIII	0/0/0	4/0/38	15/0/42	56/0/71	74/0/84	86/0/96	101/0/102	102/0/102
XIV	0/0/0	5/0/31	32/0/46	65/0/72	86/0/83	90/0/96	101/0/101	102/0/101
XV	0/0/0	4/0/30	35/0/45	65/0/70	86/0/80	93/0/94	100/0/100	101/0/102
XVI	0/0/0	0/0/0	30/0/38	49/0/49	78/0/69	86/0/88	93/0/96	100/0/100
XVII	0/0/0	0/0/0	0/0/0	16/0/13	21/0/46	56/0/68	73/0/80	86/0/93
XX	0/0/0	6/0/30	31/0/36	50/0/50	76/0/70	86/0/89	100/0/100	100/0/101
XXI	0/0/0	6/0/14	30/0/46	62/0/70	86/0/90	96/0/100	100/0/102	103/0/102

ity of the prepared compounds to form aggregates to a degree controlled by a solvating ability of the medium. Such aggregates have been described for tetraalkylammonium salts [6—8]. In contrast with chloroacetic acid esters [4], it seems probable that the observed sensitivity of wavenumbers $\nu(C=O)$ of the benzothiazolium salts to the nature of alkoxy group accounts not only for the inductive effect of a substituent but also for weak, nonbonding interactions formed as a result of the aggregation of molecules. These effects will be a topic of our further, more detailed investigation.

The biological activity of the compounds under study was examined on a model organism of *Euglena gracilis*; their antibacterial and antifungal properties and also effect on the growth of the root system of vetch were also tested. Unicelled organism *Euglena gracilis* can live as an autotroph, heterotroph or mixotroph. Chemicals can affect either the growth of *Euglena gracilis* culture or can interfere with the cell chloroplast organelle. Studying both forms of action, it was found out that all the tested compounds have an effect on the cells division of *Euglena gracilis* and the synthesis of chlorophyll as well. The results summed up in Table 3 clearly demonstrate the inhibition activity at higher concentrations on both processes. Lower concentrations have either no effect or some compounds slightly stimulate both processes. Some relationships between the chemical structure and the activity can be drawn from these results. The compounds *I—X* bearing methyl, allyl, propargyl or benzyl group at the position 3 are relatively powerful inhibitors. Concentration of 100 $\mu g/cm^3$ is 100 % lethal and even the concentration of 0.1 $\mu g/cm^3$ slightly inhibits both processes. The compounds *XI—XVIII* and *XXI*, to the contrary, are less toxic for *Euglena gracilis*, nay, stimulate the cells division and the synthesis of chlorophyll at concentrations of 0.1—1 $\mu g/cm^3$. Higher sublethal concentrations of the compounds *I—X* have the significant inhibitory effect on chlorophyll. After the inhibitor had been removed by washing up and the cells had been inoculated on a heterotrophic medium, 100 % green population was developed. In the case of compounds *I*, *VIII*, and *IX* also white colonies were present, though in amounts not exceeding 6 % of the total number of colonies.

Tests on the antibacterial activity resulted in finding out that the compounds are preferentially active against gram-positive strains. As Table 4 shows, they are most effective against *Staphylococcus aureus* sensitive to antibiotics and also against *Staphylococcus aureus* resistant to penicillin and ampicillin. There is a minute or no activity at all against gram-negative strains. *Escherichia coli* and *Pseudomonas aeruginosa* were inhibited neither by the highest concentration tested (200 $\mu g/cm^3$) nor under conditions of the dilution test. The higher activity against gram-positive bacterial strains has also been found in other classes of benzothiazolium salts reported earlier [9]. The antifungal activities (Table 5) are

Table 4

Antibacterial activity of the synthesized compounds

Compound	Minimum inhibitory concentration μg/disc				
	1	*2*	*3*	*4*	*5*
I	50	50	200	200	200
II	50	50	50	200	200
III	50	50	50	200	200
IV	50	50	50	200	200
V	200	200	200	200	200
VI	50	50	50	200	200
VII	50	50	200	200	200
VIII	50	50	50	200	200
IX	12.5	12.5	12.5	200	200
X	12.5	12.5	12.5	200	200
XI	200	200	200	200	200
XII	50	50	200	200	200
XIII	50	50	200	200	200
XIV	50	50	200	200	200
XV	50	50	200	200	200
XVI	12.5	12.5	50	200	200
XVII	50	50	50	200	200
XX	200	200	200	200	200
XXI	200	200	200	200	200

1 Staphylococcus aureus 29/58; 2. Staphylococcus aureus 2560; 3. Bacillus subtilis 18/66; 4. Escherichia coli 326/71; 5. Pseudomonas aeruginosa 10662.

interesting, too. The most sensitive strain to the prepared compounds, *Candida pseudotropicalis* (yeast), is inhibited by compounds *I*—*X* even at 0.1 μg/cm^3 concentration. The least sensitive strain is *Chaetomium globbosum*, while fungistatical effect against *Microsporum gypseum* was observed at the concentration of 5 μg/cm^3. Also the rest of compounds exhibits relatively satisfactory activity against the yeast strain. The growth-regulation tests were carried out on seeds of vetch (*Vicia sativa*, var. *Fatima*). The extension of roots in length is one of the important features of plants. The tested derivatives, concerning their structure and concentrations applied, affected the growth of primary vetch roots in length to a various degree. Ten derivatives caused the inhibitory effect in a wide range of concentrations (10^{-3}—10^{-13} mol dm^{-3}) with the maximum of inhibition at $c = 10^{-3}$ mol dm^{-3}. The inhibition of roots growth at this concentration varied from 5.97 % up to 53.76 % (Table 6). The additional nine derivatives showed

Table 5

Antifungal activity of 2-styryl-3-R-benzothiazolium salts

Compound	Fungicidal/statical concentration μg/cm³			
	1	*2*	*3*	*4*
I	50/5	200/50	400/200	10/1
II	50/5	200/50	400/200	1/0.1
III	50/5	50/5	200/50	1/0.1
IV	50/5	50/5	200/50	1/0.1
V	50/5	200/50	200/50	1/0.1
VI	50/5	200/50	400/200	1/0.1
VII	50/5	200/50	400/200	1/0.1
VIII	50/5	200/50	400/200	1/0.1
IX	25/5	50/5	200/50	1/0.1
X	25/5	50/5	200/50	1/0.1
XI	200/50	200/50	400/200	50/10
XII	200/50	400/200	400/200	50/10
XIII	200/50	400/200	400/200	50/10
XIV	200/50	400/200	400/200	50/10
XVI	50/5	200/50	400/200	50/10
XVII	200/50	400/200	400/200	200/50
XXI	400/200	400/200	400/200	200/50

1. Microsporum gypseum; 2. Penicillium funiculosum; 3. Chaetomium globbosum; 4. Candida pseudotropicalis.

also an inferior stimulation activity due to low concentrations. The most effective derivative of the presented benzothiazolium salts is 2-styryl-3-propoxycarbonylmethylbenzothiazolium bromide (*XV*). This compound stimulates the growth within the range of concentrations of 10^{-7}—10^{-11} mol dm^{-3} with the maximum of 16.51 % at $c = 10^{-11}$ mol dm^{-3}, and acts as an inhibitor in the range of $c = 10^{-3}$—10^{-4} mol dm^{-3}, with the maximum of inhibition being 53.03 % at $c = 10^{-3}$ mol dm^{-3}. Table 7 presents the values obtained in the stimulation area as well as the levels of significance. The tests did not prove any positive correlation between the chemical structure of the studied compounds and the stimulation/inhibition activity on the plant growth. For instance, the compound *XI* displays a minute activity in both areas. Replacement of hydrogen in the carboxyl group for methyl (*XII*) or ethyl (*XIII*) increases the inhibitory effect enormously. Allyl group (*XVII*) demonstrates the inhibitory effect in the whole scale of concentrations. Propyl group (*XV*) has the excellent stimulatory and inhibitory effect, while heptyl group (*XX*) represents approximately 50 % of

Table 6

Growth-regulation activity of the synthesized compounds on vetch

Compound	Stimulation %	c mol dm^{-3}	Inhibition %	c mol dm^{-3}
I	7.95	10^{-7}	21.52	10^{-3}
II	2.45	10^{-9}	44.64	10^{-3}
III			12.02	10^{-3}
IV			37.28	10^{-3}
V	1.02	10^{-7}	42.14	10^{-3}
VI			5.97	10^{-3}
VII			49.56	10^{-3}
VIII			49.28	10^{-3}
IX			33.36	10^{-3}
X			30.23	10^{-3}
XI	4.34	10^{-13}	1.77	10^{-3}
XII			42.36	10^{-3}
XIII			32.14	10^{-3}
XIV	5.05	10^{-13}	52.27	10^{-3}
XV	16.51	10^{-11}	53.03	10^{-3}
XVI	4.11	10^{-9}	14.71	10^{-3}
XVII			53.76	10^{-3}
XX	7.48	10^{-9}	17.04	10^{-3}
XXI	7.24	10^{-5}	46.54	10^{-3}
IAA	10.20	10^{-12}	39.69	10^{-6}
2,4-D	8.74	10^{-9}	45.53	10^{-5}
CCC			4.38	10^{-3}

Stimulation and inhibition were determined in respect to a control experiment performed with distilled water.

the propyl derivative (*XV*) activity. One can state unambiguously that the replacement of I^- for ClO_4^- or BF_4^- shifts the activity towards the inhibition area in the whole concentration scale.

Experimental

Melting points were determined on a Kofler hot-stage apparatus and the analytical data of the synthesized compounds are presented in Table 1. IR spectra (Table 2) were measured in nujol on a Perkin—Elmer 180 instrument calibrated with the standard spectrum of polystyrene. The wavenumbers were read with the accuracy of $\pm 2\,cm^{-1}$. UV spectra were taken on a Perkin—Elmer 450 spectrometer in acetonitrile

Table 7

Stimulation activity of 2-styryl-3-propoxycarbonylmethylbenzothiazolium bromide (*XV*)

c / mol dm^{-3}	Length of roots / mm		Stimulation / %	t
	$\bar{x}$	$s(\bar{x})$		
C	24.95	± 0.47	—	—
10^{-11}	29.07	± 0.36	16.51	4.79
10^{-9}	27.06	± 0.59	8.46	2.80
10^{-7}	27.90	± 0.72	11.82	4.98
			$P(0.05) = 2.31$	
			$P(0.01) = 3.36$	

C — control; $\bar{x}$ — arithmetic mean; $s(\bar{x})$ — standard error of arithmetic mean; t — significance; $P(0.05)$ — level of significance; $P(0.01)$ — level of high significance.

($c = 10^{-4}$ mol dm^{-3}). ^{1}H NMR spectra were measured on a Tesla 487 instrument in deuterated dimethyl sulfoxide with HMDSO as an internal standard.

The activity tests against *Euglena gracilis* were performed on the strain *Z* which was maintained on a heterotrophic proteozo-peptone-triptonic medium at the temperature of (26 ± 2) °C under permanent illumination. The effect of the tested compounds on the cells division of *Euglena gracilis* was investigated in a liquid cultivation medium in which the specific concentration of a compound was prepared. After 120 h the following was determined: a) the number of cells by a PICOSCAL-PS-4 instrument, b) the content of chlorophyll by *Arnon*'s method [10], c) potential inductions of white mutants by inoculating on a heterotrophic medium impregnated with agar; the presence of green and white colonies (bleaching activity) was established after additional 10 days cultivation on light. Nondeveloped colonies indicated the lethal effect at a particular concentration.

The following strains were involved in the antibacterial and antifungal activity studies: *Staphylococcus aureus Mau 29/58* (sensitive to antibiotics), *Staphylococcus aureus Mau 2560* (resistant to penicillin and ampicillin), *Bacillus subtilis B.s. 18/66*, *Escherichia coli E.c. 326/71* and *Pseudomonas aeruginosa*. The tests were accomplished by the plate-diffusion method in a Mueller—Hinton agar. The compounds were placed on circles of a chromatographic paper in defined concentrations. The effect was estimated in respect of the areas of the inhibition zone developed after cultivation at 37 °C for 24 h. The inhibitory concentrations (MIC) given in Table 4 represent such concentrations that created still visible and measurable zone of the growth inhibition. The antifungal activity was tested against the strains of *Microsporum gypseum*, *Penicillium funiculosum 1818*, *Chaetomium globbosum 358*, and *Candida pseudotropicalis C 126*. The effect was determined by the test-tube dilution method in a Sabourand medium.

2-Styryl-3-methylbenzothiazolium methyl sulfate (I)

To a solution of 2-styrylbenzothiazole (2.3 g; 0.01 mol) in 15 cm^3 of anhydrous acetone, dimethyl sulfate (1.8 g; 0.015 mol) was added. The mixture was heated for 2 h at reflux temperature and then left to stand at room temperature for 24 h. The crystals separated were filtered off and washed with acetone.

2-Styryl-3-methylbenzothiazolium iodide (II)

2-Styrylbenzothiazole (2.3 g; 0.01 mol), 15 cm^3 of anhydrous acetonitrile, and methyl iodide (2.1 g; 0.015 mol) were heated at 75—80 °C (bath temperature) for 18 h. The crystals were washed with acetone and crystallized from a mixture of anhydrous methanol—acetone (volume ratio = 2 : 1).

2-Styryl-3-methylbenzothiazolium perchlorate (III) and tetrafluoroborate (IV)

2-Styryl-3-methylbenzothiazolium iodide (*II*) (7.5 g; 0.02 mol) was dissolved in 30 cm^3 of warm (40—50 °C) methanol — water mixture (r_V = 1 : 1). A solution of $KClO_4$ (KBF_4) (0.04 mol) in 20 cm^3 of 40—50 °C warm water was gradually added with stirring. The crystalline product was washed with water and purified by crystallization from methanol.

2-Styryl-3-benzylbenzothiazolium bromide (V)

2-Styrylbenzothiazole (2.3 g; 0.01 mol), 15 cm^3 of anhydrous acetonitrile or dimethylformamide, or a mixture of dimethylformamide and acetone (r_V = 2 : 1) and benzyl bromide (2.5 g; 0.015 mol) were heated at 70—80 °C (bath temperature) for 24 h. On cooling, the product usually separates in a crystal form. If not, 1—2 cm^3 of the solution is placed in a test-tube, the same volume of ether or acetone is added and the crystallization is induced by scratching the inside of the test-tube. The content of the test-tube is returned to the reaction mixture. Isolated solid is crystallized from methanol. Alternatively, if no crystals separate on cooling, anhydrous ether or acetone is added to the solution until turbidity occurs.

2-Styryl-3-benzylbenzothiazolium perchlorate (VI), tetrafluoroborate (VII), and nitrate (VIII)

2-Styryl-3-benzylbenzothiazolium bromide (*V*) (4.0 g; 0.01 mol) was dissolved in 30 cm^3 of 40—50 °C warm water and $KClO_4$ (KBF_4 or KNO_3) (0.02 mol) dissolved in

20 cm^3 of water of the same temperature was added gradually with stirring. After washing the crystals with water, they were satisfactorily pure according to the results of elemental analysis.

2-Styryl-3-allylbenzothiazolium bromide (IX) and 2-styryl--3-propargylbenzothiazolium bromide (X)

2-Styrylbenzothiazole (2.3 g; 0.01 mol), 10 cm^3 of acetonitrile, and allyl bromide (propargyl bromide) (0.015 mol) were heated at 75—80 °C (bath temperature) for 20 h. After cooling, the crystalline product was washed with acetone.

2-Styryl-3-carboxymethylbenzothiazolium bromide (XI) and esters (XII—XXI)

2-Styrylbenzothiazole (2.3 g; 0.01 mol), 10 cm^3 of acetonitrile, and bromoacetic acid (corresponding ester) (0.015 mol) were heated at 70—75 °C (bath temperature) for 16 h. The crystals were filtered off and impurities were removed by extraction with boiling anhydrous ethanol.

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