Benzothiazole compounds
XXXIV. Preparation of (*E*)-3-(2-R-vinyl)-2-benzothiazolinones and investigation of their growth-regulating activity

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The synthesis of (*E*)-3-(2-R-vinyl)-2-benzothiazolinones by the Wittig reaction from (2-oxo-3-benzothiazolinylmethyl)triphenylphosphonium chloride and substituted aromatic aldehydes in the presence of triethylamine or sodium methoxide is described. The *E* configuration of the compounds was proved and *Z* isomers were prepared photochemically. Electron structure and geometry of (*Z*)-3-(2-phenylvinyl)-2-benzothiazolinone was studied by the CNDO/2 and PCILO methods. The compounds exhibited growth-regulating activity on *Vicia sativa* L., *cv.* Solarka and *Triticum aestivum* L.

Описан синтез (*E*)-3-(2-R-винил)-2-бензотиазолинонов с помощью реакции Виттига из (2-оксо-3-бензотиазолинилметил)трифенилфосфоний хлорида и замещенных ароматических альдегидов в присутствии триэтиламина или метоксида натрия. Была доказана *E* конфигурация полученных соединений, и *Z* изомеры были получены путем фотохимической реакции. Электронная структура и геометрия (*Z*)-3-(2-фенилвинил)-2-бензотиазолинона исследовались с помощью методов CNDO/2 и PCILO. Полученные вещества проявляли способность регулировать рост *Vicia sativa* L., *cv.* Solarka и *Triticum aestivum* L.

3-Substituted 2-benzothiazolinones have been studied from the viewpoint of their plant growth-regulating activity and have been the subjects of many patents [1—3]. The aim of the present work was to synthesize (*E*)-3-(2-R-vinyl)-2-benzothiazolinones, to determine their configuration, and ascertain their effects on the growth of *Vicia sativa* L., *cv.* Solarka and *Triticum aestivum* L.

(*E*)-3-(2-R-vinyl)-2-benzothiazolinones *I*—*XVII* (Table 1) were prepared by the Wittig reaction, when 3-(chloromethyl)-2-benzothiazolinone was treated with triphenylphosphine affording (2-oxo-3-benzothiazolinylmethyl)triphenyl-

Table 1

Characterization of the synthesized compounds

Compound	R	Formula	M_r	w_i(calc.)/% w_i(found)/%				Yield	M.p.
				C	H	N	S	%	°C
I	C_6H_5	$C_{15}H_{11}NOS$	253.32	71.15	4.43	5.53	12.64	30	91—92.5
				71.16	4.43	5.62	12.71		
II	$2\text{-}NO_2C_6H_4$	$C_{15}H_{10}N_2O_3S$	298.32	60.39	3.37	9.39	10.71	46	157—160
				60.15	3.25	9.15	10.53		
III	$3\text{-}NO_2C_6H_4$	$C_{15}H_{10}N_2O_3S$	298.32	60.39	3.37	9.39	10.71	37	192—195
				60.58	3.33	9.16	10.54		
IV	$4\text{-}NO_2C_6H_4$	$C_{15}H_{10}N_2O_3S$	298.32	60.39	3.37	9.39	10.71	67	209—212
				60.30	3.32	9.20	10.50		
V	$2\text{-}ClC_6H_4$	$C_{15}H_{10}ClNOS$	287.77	62.62	3.50	4.86	11.14	23	89—91
				62.70	3.32	4.66	11.20		
VI	$4\text{-}ClC_6H_4$	$C_{15}H_{10}ClNOS$	287.77	62.62	3.50	4.86	11.14	49	132—135
				62.35	3.66	4.72	10.96		
VII	$3,4\text{-}Cl_2C_6H_3$	$C_{15}H_9Cl_2NOS$	322.21	55.91	2.81	4.34	9.95	57	220—223
				55.64	2.64	4.32	9.83		
VIII	$2\text{-}OCH_3C_6H_4$	$C_{16}H_3NO_2S$	283.35	67.83	4.62	4.94	11.31	50	65—67.5
				68.00	4.59	4.99	11.38		

Table 1 (Continued)

Compound	R	Formula	M_r	w_i(calc.)/% w_i(found)/%				Yield	M.p.
				C	H	N	S	%	°C
IX	$4\text{-}OCH_3C_6H_4$	$C_{16}H_{13}NO_2S$	283.35	67.83	4.62	4.94	11.31	32	78—80
				67.70	4.50	4.80	11.16		
X	$2,4\text{-}(OCH_3)_2C_6H_3$	$C_{17}H_{15}NO_3S$	313.37	65.17	4.82	4.47	10.23	26	65—68
				65.10	4.87	4.37	10.23		
XI	$4\text{-}N(CH_3)_2C_6H_4$	$C_{17}H_{16}N_2OS$	296.39	68.88	5.77	9.45	10.81	34	144—146
				68.73	5.41	9.55	10.77		
XII	$4\text{-}CH_3CONHC_6H_4$	$C_{17}H_{14}N_2O_2S$	310.37	65.80	4.54	9.02	10.30	68	225—228
				65.92	4.48	8.94	10.28		
XIII	$3,4\text{-}(O_2CH_2)C_6H_3$	$C_{16}H_{11}NO_3S$	297.33	64.64	3.72	4.71	10.78	26	107—109
				64.41	3.96	4.45	10.50		
XIV	2-Fu[a]	$C_{13}H_9NO_2S$	243.28	64.17	3.72	5.75	13.18	34	79—82
				64.60	3.70	5.79	13.20		
XV	3-Pyr[a]	$C_{14}H_{10}N_2OS$	254.31	66.12	3.96	11.01	12.60	44	137—140
				66.27	3.94	10.98	12.50		
XVI	$C_6H_5CH{=}CH$	$C_{17}H_{13}NOS$	279.36	73.07	4.69	5.01	11.47	50	164—167
				73.45	4.73	5.02	11.47		
XVII	$5\text{-}(4\text{-}CH_3C_6H_4)\text{-}2\text{-}Fu$	$C_{20}H_{15}NO_2S$	333.42	72.05	4.53	4.20	9.61	45	143—145
				71.82	4.56	4.20	9.56		

a) Pyr — pyridyl, Fu — furyl.

phosphonium chloride which was condensed with aromatic aldehydes in the presence of triethylamine or sodium methoxide. The synthesis was carried out in absolute methanol under reflux.

The structure of the prepared compounds was proved by IR spectra measured in solid state (in paraffin oil). The wavenumbers of the characteristic vibrations of compounds *I—XVII* are listed in Table 2.

The spectra of all compounds show an intense absorption band due to the C=O stretching vibration in the region of $\tilde{\nu} = 1670—1700\ \mathrm{cm}^{-1}$, characteristic of 2-benzothiazolinone derivatives [4]. A band of moderate intensity in the range of $\tilde{\nu} = 1635—1655\ \mathrm{cm}^{-1}$ is relevant to the C=C stretching vibration of substituted vinyl group. Another band of lower intensity occurring in the region of $\tilde{\nu} = 1580—1600\ \mathrm{cm}^{-1}$ can be assigned to the C=C stretching vibrations in aromatic and heteroaromatic rings. The presence of an intense band of out-of-plane bending vibration τ(CH) in the region of $\tilde{\nu} = 930—975\ \mathrm{cm}^{-1}$ indicates that the 3-(2-R-vinyl)-2-benzothiazolinones are of *E* configuration with regard to the plane of the C=C bond of substituted vinyl group. The substitution in the benzene ring of benzothiazolinone skeleton and of the group R is unambiguously proved by characteristic strong bands of out-of-plane bending and ring vibrations in the region of $\tilde{\nu} = 690—895\ \mathrm{cm}^{-1}$ The intense absorption bands at $\tilde{\nu} = 1025—1050\ \mathrm{cm}^{-1}$ in the spectra of compounds *VIII—X* and *XIII* correspond to C—O or C—O—C stretching vibrations. Nitro derivatives *II—IV* show two strong bands in the regions of $\tilde{\nu} = 1340—1350$ and $1515—1525\ \mathrm{cm}^{-1}$ due to the symmetrical and asymmetrical stretching vibrations of NO_2 group. The compounds *XIV*, *XV*, and *XVII*, containing a heterocyclic ring in the moiety R, show characteristic out-of-plane bending and ring vibration bands in the range of $\tilde{\nu} = 705—950\ \mathrm{cm}^{-1}$ The system of conjugated double bonds C=C—C=C in the compound *XVI* is exhibited at $\tilde{\nu} = 1620$ and $1630\ \mathrm{cm}^{-1}$ as a doublet due to the symmetrical and asymmetrical stretching vibrations. In the case of compound *XII* the acetylamino group is proved by the presence of absorption bands of ν(C=O) and ν(N—H) vibrations at $\tilde{\nu} = 1675$ and $3330\ \mathrm{cm}^{-1}$, respectively.

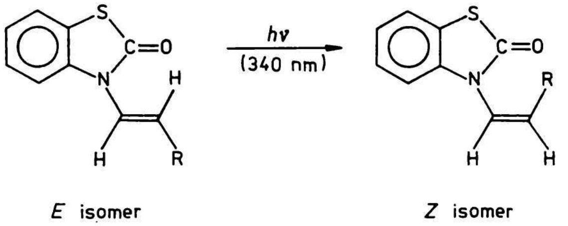
The synthesized *E* isomers of 3-(2-R-vinyl)-2-benzothiazolinones show a strong absorption band in the near UV region which bathochromically shifts to longer wavelengths with increasing solvent polarity and electron-donating ability of the substituent R (Table 3). These changes in UV spectra indicate that the long-wave absorption band is due to a $\pi—\pi^*$ transition. Depending on the nature of both the substituent and the solvent, this $\pi—\pi^*$ singlet more or less overlaps the $n—\pi^*$ singlet. By analogy with stilbenes [5] and other derivatives with styrene chromophore, *Z* isomers of 3-(2-R-vinyl)-2-benzothiazolinones were prepared photochemically. However, they were not isolated (Scheme 1).

The rate of isomerization and the yield of the *Z* isomers depend on the nature

Table 2

Characteristic IR spectral data of (*E*)-3-(2-R-vinyl)-2-benzothiazolinones

Compound	$\tilde{\nu}/\mathrm{cm}^{-1}$					
	ν(C=O)	ν(C=C)	$\nu(\mathrm{C}\cdots\mathrm{C})_{\mathrm{arom}}$	τ(CH)	ω(CH) and ring vibrations	Other vibrations
I	1685	1645	1595	950	750 (4H + 5H), 690 (5H)	
II	1675	1640	1587	945	735 (4H)	$\nu_{as}(\mathrm{NO_2})$ 1520, $\nu_s(\mathrm{NO_2})$ 1350
III	1675	1645	1595	955	825 (1H), 805 (3H), 750 (4H)	$\nu_{as}(\mathrm{NO_2})$ 1525, $\nu_s(\mathrm{NO_2})$ 1350
IV	1680	1655	1590	945	860 (2H), 755 (4H)	$\nu_{as}(\mathrm{NO_2})$ 1515, $\nu_s(\mathrm{NO_2})$ 1340
V	1690	1645	1590	960	745 (4H)	
VI	1680	1650	1590	960	820 (2H), 750 (4H)	
VII	1675	1650	1590	955	895 (1H), 815 (2H), 750 (4H)	
VIII	1685	1645	1585	955	750 (4H)	ν(C—O) 1030
IX	1685	1650	1590	960	810 (2H), 760 (4H)	ν(C—O) 1030
X	1685	1655	1580	945	842 (1H), 830 (2H), 740 (4H)	ν(C—O) 1025
XI	1675	1635	1600	960	820 (2H), 760 (4H)	
XII	1695	1645	1595	940	810 (2H), 745 (4H)	ν(C=O) 1675, ν(N—H) 3330
XIII	1680	1655	1595	940	855 (1H), 810 (2H), 750 (4H)	ν(C—O—C) 1050
XIV	1700	1655	1585	940	750 (4H)	γ(2-Fu) 940, 855, 735
XV	1670	1645	1585	950	745 (4H)	γ(3-Pyr) 942, 790, 705
XVI	1675	—	1590	975	750 (5H), 740 (4H), 695 (5H)	ν(C=C—C=C) 1630, 1620
XVII	1670	1650	1585	930	820 (2H), 745 (4H)	γ(2,5-Fu) 950, 925, 785



Scheme 1

of substituent R (Table 3). We assume that the isomerization starts from the triplet state. After absorption of the light, an intersystem crossing occurs giving rise to the $n-\pi^*$ triplet from which, presumably, the $\pi-\pi^*$ triplet is formed by intramolecular energy transfer. Such an intramolecular transfer of energy has been noticed and described [6, 7]. The $\pi-\pi^*$ triplet is then the starting point of isomerization. A substituent can influence triplet energy of both $\pi-\pi^*$ and $n-\pi^*$ transitions. Due to better overlapping of π orbitals, the singlet—triplet splitting of $\pi-\pi^*$ transitions is much more sensitive to the substituent or solvent

Table 3

Spectral characteristics and conversion of photochemical isomerization of 3-(2-R-vinyl)-2-benzothiazolinones

Compound	*E* Isomer	*Z* Isomer		
	λ_{max} / nm	$\log \varepsilon(\lambda_{max})$ / $m^2\,mol^{-1}$	Conversion / %	Time / s
I	284	3.24	40	180
II	246	3.20	42	160
III	280	3.09	40	160
IV	340	2.98	45	90
V	287	3.15	35	180
VI	288	3.23	40	180
VII	288	2.90	40	120
VIII	304	3.18	25	250
IX	284	3.25	5	3600
X	308	2.94	4	1800
XI	320	3.37	0	180
XII	299	3.06	30	3600
XIII	313	3.02		
XIV	302	3.15		
XV	298	3.17		
XVI	317	3.24		
XVII	343	3.21		

changes than singlet—triplet splitting of n—π^* transitions. In our compounds with electron-withdrawing or slightly electron-donating substituents, the difference between n—π^* and π—π^* triplets is, supposedly, small. In such a case an efficient energy transfer occurs giving rise to a high yield of *Z* isomers. On the contrary, stronger electron-donating groups cause higher energic difference between the n—π^* and π—π^* triplets and, consequently, the yields of *Z* isomers are lower. For the derivatives *IX*, *X*, and *XII* no isomerization could be detected.

The structure of the *Z* isomers was proved by IR spectroscopy. The spectra of (*Z*)-3-(2-R-vinyl)-2-benzothiazolinones did not show considerable absorption in the region of $\tilde{\nu} = 930$—$975\ \text{cm}^{-1}$, which would be characteristic of out-of-plane bending vibration of the group CH=CH with *E* configuration [4]. On the other hand, there is a band due to the τ(CH) vibration in the region of $\tilde{\nu} = 700$—$720\ \text{cm}^{-1}$, which can be regarded as a proof of *Z* configuration of the studied compounds. The wavenumbers of C=O stretching vibrations of the *Z* isomers of 3-(2-R-vinyl)-2-benzothiazolinones (measured in $CHCl_3$) fall within the interval of 1722—1725 cm^{-1} and are by 40 cm^{-1} higher than those of *E* isomers [4]. This fact is most probably caused by break of coplanarity between the thiazolinone ring and the substituted vinyl moiety. This assumption can be supported also by the fact that the wavenumbers of the C=O stretching vibra-

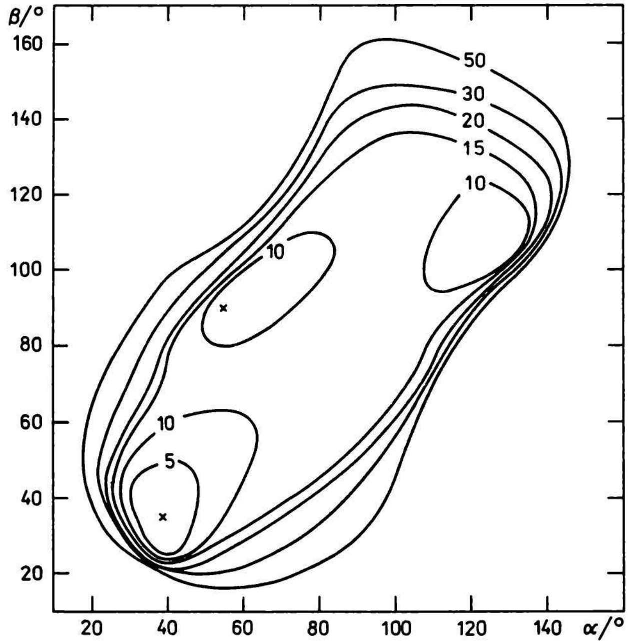
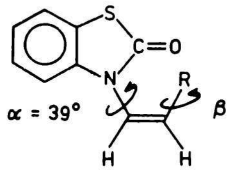


Fig. 1. Relationship between the total energy (in kJ mol^{-1}) of (*Z*)-3-(2-phenylvinyl)-2-benzothiazolinone and the dihedral angles α and β.

tions depend only very little on the nature of the substituent R. Similar, though a little smaller, increase in wavenumbers of C=O stretching vibrations ($\Delta\tilde{\nu} = 7$—$13\ \mathrm{cm^{-1}}$) has been found in *Z* isomers as compared with *E* isomers of 1,2-diphenyl-3-(X-phenyl)propenones when the conjugation between C=C and C=O bonds was disturbed [8].

The configuration on the double bond in our 3-(2-R-vinyl)-2-benzothiazolinones could not be proved by ^{1}H NMR spectra, because the signals of protons of —CH=CH— group in question are superimposed with the signals of aromatic protons.

Electron structure and geometry of a model compound of the series (*Z*)-3-(2-phenylvinyl)-2-benzothiazolinone (*I*) were studied by the CNDO/2 and PCILO methods. An isoenergetic map, constructed on the basis of PCILO calculations (Fig. 1), shows that this *Z* isomer occurs mainly in nonplanar conformation in which the substituted vinyl group is twisted out of the plane of thiazolinone ring with the dihedral angle $\alpha = 39°$



The relationship between total energy and the dihedral angle offers a possibility of find out another two relative minima corresponding with the angles $\alpha = 55°$ and $\alpha = 123°$, the energy difference, as compared with the absolute minimum, being 7 and 6 kJ mol^{-1}, respectively. From the comparison of charge densities in the molecular diagram (Fig. 2) it follows that the conjugation between the C_6H_5—CH=CH— group and the benzothiazolinone system is disturbed, which results in increasing of the wavenumbers of the C=O stretching vibrations in IR spectra (as compared with *E* isomers) and causes strong restraining of the transmission of electronic effects from the substituent R towards the C=O group.

The compounds were tested on *Vicia sativa* L., *cv.* Solarka and *Triticum aestivum* L. for their growth-regulating activity. It was found that they caused various growth effects when applied on the seeds of *Vicia sativa* L., *cv.* Solarka in the concentrations of 10^{-13} to $10^{-3}\ \mathrm{mol\ dm^{-3}}$ (Table 4). As stimulants, the compounds (*E*)-3-[2-(4-chlorophenyl)vinyl]-2-benzothiazolinone (*VI*), (*E*)-3-[2-(3,4-dichlorophenyl)vinyl]-2-benzothiazolinone (*VII*), (*E*)-3-[2-(4-methoxyphenyl)vinyl]-2-benzothiazolinone (*IX*), (*E*)-3-[2-(2,4-dimethoxyphenyl)vinyl]-2-benzothiazolinone (*X*), and (*E*)-3-[2-(4-acetamidophenyl)vinyl]-2-benzothiazolinone (*XII*) are comparable with the standard, *β*-indolylacetic acid (IAA).

The difference in the activity of isomeric compounds *V* and *VI* is interesting. The compound (*E*)-3-[2-(2-chlorophenyl)vinyl]-2-benzothiazolinone (*V*) showed the stimulating activity by 45 % lower, but the inhibitory effect by 31 % higher than *VI*. A similar relationship was found between the compounds *VIII* and *IX*. The stimulating activity of (*E*)-3-[2-(2-methoxyphenyl)vinyl]-2-benzothiazolinone (*VIII*) was by 42 % lower than that of *IX*. Two methoxy groups in *X* caused an increase in stimulating activity by 96 % as compared with compound *IX*. The stimulating activity of other compounds is low, approximately at the same level.

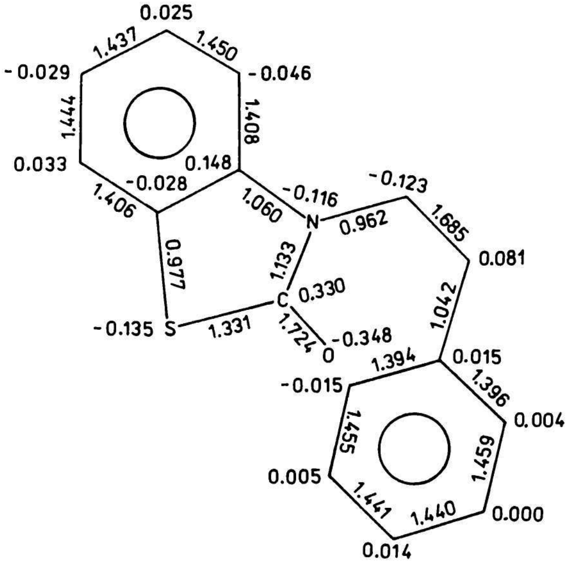


Fig. 2. Molecular diagram of the Wiberg indices and charge magnitudes of (*Z*)-3-(2-phenylvinyl)-2-benzothiazolinone.

Compounds *II* and *IV* were active only in the inhibitory area. The inhibitory activity of all compounds is not interesting from the practical point of view, because it is achieved only with high concentrations. Three compounds were active on the other tested plant *Triticum aestivum* L. The highest stimulating effect was found with (*E*)-3-[2-(4-nitrophenyl)vinyl]-2-benzothiazolinone (*IV*) that gave negative results in this respect when tested on *Vicia sativa* L., *cv.* Solarka. Good activity was found also with (*E*)-3-[2-(3-nitrophenyl)vinyl]-2-benzothiazolinone (*III*) and (*E*)-3-(2-styrylvinyl)-2-benzothiazolinone (*XVI*) in stimulating area, the other compounds exhibited only below-average activity. The results are summarized in Table 4.

Table 4

Growth-regulating activity of the synthesized compounds

Compound	Stimulation			Inhibition		
	Δl/mm	%[a]	c/(mol dm^{-3})	$-\Delta l$/mm	%[a]	c/(mol dm^{-3})
			Vicia sativa L., *cv.* Solarka			
I	1.56	4.95	10^{-5}	6.83	21.69	10^{-3}
II				10.83	32.43	10^{-3}
III	1.79	6.86	10^{-7}	6.64	25.47	10^{-3}
IV				12.47	48.83	10^{-3}
V	1.87	7.15	10^{-13}	16.13	61.73	10^{-3}
VI	3.64	12.89	10^{-5}	5.49	19.46	10^{-3}
VII	3.36	10.81	10^{-}	4.06	14.81	10^{-3}
VIII	1.26	4.52	10^{-9}	9.94	35.67	10^{-3}
IX	3.33	10.53	10^{-11}	6.40	20.26	10^{-3}
X	5.67	20.67	10^{-7}	3.77	13.75	10^{-3}
XI	1.59	5.70	10^{-7}	8.01	24.66	10^{-3}
XII	3.81	13.29	10^{-}	2.88	10.05	10^{-3}
XIII	2.14	6.70	10^{-11}	5.07	15.88	10^{-3}
XIV	1.87	6.23	10^{-5}	13.53	45.10	10^{-3}
XVI	1.20	4.01	10^{-9}	6.07	20.33	10^{-3}
IAA	3.10	12.99	10^{-12}	18.55	77.78	10^{-6}
2,4-D	4.95	20.00	10^{-9}	23.30	94.15	10^{-5}
CCC				3.85	11.23	10^{-3}
			Triticum aestivum L.			
I	0.50	9.20	10^{-7}	1.69	31.13	10^{-3}
II	0.17	3.13	10^{-11}	1.35	24.87	10^{-3}
III	0.61	11.23	10^{-5}	1.83	33.71	10^{-3}
IV	1.10	20.25	10^{-}	1.85	34.07	10^{-3}
V	0.25	5.16	10^{-9}	1.06	21.91	10^{-3}
VI	0.17	3.03	10^{-5}	1.45	25.85	10^{-3}
VII	0.29	5.99	10^{-7}	1.01	20.87	10^{-3}
VIII				1.78	31.73	10^{-3}
IX	0.19	3.92	10^{-4}	0.59	31.73	10^{-3}
X				1.61	28.70	10^{-3}
XI				2.38	42.43	10^{-3}
XII	0.29	5.16	10^{-4}	1.70	30.31	10^{-3}
XIII	0.49	9.02	10^{-7}	1.81	33.34	10^{-3}
XIV	0.35	7.23	10^{-5}	1.40	28.93	10^{-3}
XVI	0.62	12.80	10^{-4}	0.64	13.85	10^{-3}
IAA	5.93	100.33	10^{-5}	2.77	46.72	10^{-3}
2,4-D	2.56	51.09	10^{-5}	2.01	40.12	
CCC				1.75	32.35	10^{-3}

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

a) Comparison with the control (blank) test.

Experimental

Melting points determined on a Kofler micro hot-stage and analytical data of the synthesized compounds are given in Table 1. IR spectra of *E* and *Z* isomers were measured on a Perkin—Elmer 567 instrument in the region of $\tilde{\nu} = 400—4000\ \text{cm}^{-1}$ in suspension in paraffin oil or in $CHCl_3$. KBr cuvettes with the thickness of absorbing layer of suspension 0.02 or 0.1 mm were used. The wavenumber scale of the instrument was calibrated using a comparative spectrum of polystyrene. The readings of the wavenumbers were taken with $\pm 2\ \text{cm}^{-1}$ accuracy. UV spectra were recorded in chloroform using a Perkin—Elmer 450 spectrophotometer.

Growth tests

In the tests with *Triticum aestivum* L., grains were swollen in distilled water for 2—3 h at room temperature. Germination was accomplished in dark at 25 °C. When the coleoptiles reached 20—25 mm, a 3 mm segment was cut out of each, 2 mm from the tip. The coleoptile segments were kept in distilled water for 2 h and then put into the tested solutions containing 2 % sucrose, 10 pieces each time. After 24 h incubation at 25 °C, the coleoptiles were measured by means of a photographic enlarging apparatus. The differences were expressed percentually, based on the control test, and the significance was calculated according to the t-test. The whole experiment was carried out under red light. The solutions were diluted so that they formed the concentration scale of 10^{-13}—$10^{-3}\ \text{mol dm}^{-3}$; 2 % sucrose solution was used for the control test. This biotest is sensitive not only to auxinoid compounds but also to inhibitory ones that hamper the prolongation of segments.

The growth test on *Vicia sativa* L., *cv*. Solarka was carried out according to [9]. *β*-Indolylacetic acid (IAA), 2,4-dichlorophenoxyacetic acid (2,4-D), and 2-chloroethyltrimethylammonium chloride (CCC) were used as standards.

(2-Oxo-3-benzothiazolinylmethyl)triphenylphosphonium chloride

3-Chloromethyl-2-benzothiazolinone (30 g; 0.15 mol) and triphenylphosphine (39.3 g; 0.15 mol) were dissolved in anhydrous benzene (120 cm^3). The reaction mixture was refluxed for 2 h. Benzene was evaporated under reduced pressure and anhydrous acetone was added to the residue. Crystalline product was filtered off and washed with acetone. Yield = 57.5 g (82.3 %), m.p. = 269—274 °C. For $C_{26}H_{21}ClNOPS$ (M_r = = 461.95) w_i(calc.): 67.59 % C, 4.58 % H, 3.03 % N, 6.94 % S; w_i(found): 67.34 % C, 4.70 % H, 3.12 % N, 7.15 % S.

(E)-3-(2-Phenylvinyl)-2-benzothiazolinone (I)

(2-Oxo-3-benzothiazolinylmethyl)triphenylphosphonium chloride (4.6 g; 0.01 mol) was dissolved in absolute methanol (25 cm^3) and triethylamine (1.0 g; 0.01 mol) was added. The solution was stirred and benzaldehyde (1.06 g; 0.01 mol) in methanol (10 cm^3) was added dropwise. The reaction mixture was refluxed for 5 h. After cooling, water (15—20 cm^3) was added. The product was crystallized from ethanol.

(E)-3-[2-(2-methoxyphenyl)vinyl]-2-benzothiazolinone (VIII)

Sodium (0.23 g; 0.01 mol) was added to absolute methanol (10 cm^3) and the solution was mixed with (2-oxo-3-benzothiazolinylmethyl)triphenylphosphonium chloride (4.6 g; 0.01 mol) in methanol (10 cm^3). 2-Methoxybenzaldehyde (2.0 g; 0.015 mol) was added with stirring and the mixture was refluxed for 5 h. After cooling a few drops of water were added until slight turbidity occurred. The product was crystallized from ethanol.

The compounds *I—XVII* can be synthesized using either triethylamine or sodium methoxide.

(Z)-3-(2-R-vinyl)-2-benzothiazolinones

A methanolic solution (450 cm^3) of *E* isomer of 3-(2-R-vinyl)-2-benzothiazolinone (0.4 g) was irradiated in a preparatory photochemical reactor (Simax) using 400 W mercury lamp. The course of the reaction was monitored by UV spectroscopy. The irradiation was stopped when the spectrum did not cross the isosbestic point any more.

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