

Benzothiazole Compounds

XLVI. 3,4-Disubstituted 2-Benzothiazolinones with Plant Growth Regulation Activity

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For the synthesized 3-aryloxy carbonylmethyl-2-benzothiazolinones and their 4-chloro derivatives, the growth stimulation effect was examined on *Triticum aestivum* L. The stimulation activity of 47.66 % was found in the case of 4-chloro-3-furyloxy carbonylmethyl-2-benzothiazolinone. UV and IR spectra are presented.

The results obtained in the area of plant growth stimulation for benzothiazole compounds represent a motivation for further syntheses of these materials. 4-Chloro-3-phenoxy carbonylmethyl-2-benzothiazolinone, 3-(2-methoxyphenoxy carbonylmethyl)-2-benzothiazolinone [1] and 4-chloro-3-(4-formylphenoxy carbonylmethyl)-2-benzothiazolinone [2] achieved the stimulation activity of the standard – 2,4-dichlorophenoxyacetic acid. 3-Benzyloxy carbonyl-2-benzothiazolinone [3], tested in a large scale, acts as a systemic plant growth regulator affecting the growth and development, biomass production, crop and its quality. It stimulates and promotes the growth of the root system and improves the vitality of seedlings.

The aim of this work was to examine the influence of chlorine on the benzyloxy group, the effect of various substituents on phenoxy group and structurally different ester groups on the stimulation of growth of *Triticum aestivum* L.

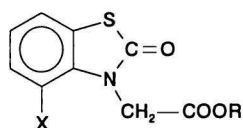
The compounds given in Table 1 were synthesized from (2-oxobenzothiazolin-3-yl)acetyl chloride or from (4-chloro-2-oxobenzothiazolin-3-yl)acetyl chloride by treatment with 2- and 4-chlorobenzyl alcohol, derivatives of phenol, cyclopentanol, cyclohexanol, furyl alcohol, α - and β -naphthol, and 8-hydroxyquinoline, respectively, in the presence of pyridine in acetone.

IR and UV spectra of the compounds under study are given in Table 2. Like in the case of the derivatives described in [1, 2], the UV spectra reflect the structural changes only to a very little extent. More significant changes have been observed in IR spectra, above all, in the region of ester carbonyl absorption ($\tilde{\nu} = 1750\text{--}1780\text{ cm}^{-1}$). The described spectra are in agreement with the general knowledge on these kinds of spectroscopy. A more or less distinguished "shoulder" of the carbonyl absorption band

has been observed which we ascribe to the intramolecular electron-donating interaction.

The stimulation activity on *Triticum aestivum* L. has been examined for the synthesized compounds in concentration of $10^{-5}\text{ mol dm}^{-3}$ (Table 3). It has been found that from 26 materials, 17 exhibit a highly significant stimulation activity (I–III, VIII–XIII, XV, XVII, XIX, XX, XXIII–XXVI), two compounds show significant activity (VII, XVIII) and seven compounds have been found to be ineffective (IV–VI, XIV, XVI, XXI, XXII). The encouraging results achieved previously [1, 2] prompted the synthesis of derivatives I–IV, i.e. the introduction of chlorine on benzyloxy group. It has been found that, with the exception for compound III, this structural change has a negative effect on the stimulation activity. The most marked change occurred in the case of compound IV which is inactive. The derivatives V and VI with strong electron-withdrawing groups in the ester part are ineffective as well. The combination of methoxy and formyl groups in 3-(2-methoxy-4-formylphenoxy carbonylmethyl)-2-benzothiazolinone (VII) provided only significant activity (12.44 %) whereas with 3-(2-methoxyphenoxy carbonylmethyl)-2-benzothiazolinone it reached 53.76 % [1] and for 3-(4-formylphenoxy carbonylmethyl)-2-benzothiazolinone, 26.97 % activity was found [2]. The introduction of allyl instead of formyl group into the position 4 in 3-(2-methoxy-4-allylphenoxy carbonylmethyl)-2-benzothiazolinone (IX) raised the stimulation activity to 44.35 %. An interesting point represents also the comparison of 3-(2-methoxyphenoxy carbonylmethyl)-2-benzothiazolinone (53.76 % activity) [1] with 3-(3,5- (XI) and 3-(2,6-dimethoxyphenoxy carbonylmethyl)-2-benzothiazolinone (XII). In XI, the activity increased to 40 %, while the value for XII was

Table 1. Characterization of the Synthesized Compounds



Compound	R	X	Formula	M_r	w(calc.)/%				Yield %	M.p./°C Solvent (φ)
					w _f (found)/%					
					C	H	N	S		
I	2-Cl—C ₆ H ₄ CH ₂	H	C ₁₆ H ₁₂ ClNO ₃ S	333.79	57.53 57.66	3.62 3.50	4.19 4.12	9.60 9.53	69	150—151 Ether—acetone (1 : 1)
II	2-Cl—C ₆ H ₄ CH ₂	Cl	C ₁₆ H ₁₁ Cl ₂ NO ₃ S	368.24	52.22 52.08	3.01 3.17	3.80 3.86	8.71 8.68	73	130—131 Acetone
III	4-Cl—C ₆ H ₄ CH ₂	H	C ₁₆ H ₁₂ ClNO ₃ S	333.79	57.53 57.38	3.62 3.54	4.19 4.02	9.60 9.47	71	153—155 Acetone
IV	4-Cl—C ₆ H ₄ CH ₂	Cl	C ₁₆ H ₁₁ Cl ₂ NO ₃ S	368.24	52.22 52.36	3.01 2.88	3.80 3.61	8.71 8.66	76	118—119 Acetone—ether (1 : 1)
V	3-CF ₃ —C ₆ H ₄	H	C ₁₆ H ₁₀ F ₃ NO ₃ S	353.32	54.44 54.31	2.85 2.91	3.93 3.87	9.08 9.28	57	151—152 Acetone—ether (3 : 1)
VI	2-COOH—C ₆ H ₄	H	C ₁₆ H ₁₁ NO ₅ S	329.33	58.35 58.47	3.35 3.24	5.85 5.71	9.74 9.58	62	175—177 Acetone
VII	2-CH ₃ O-4-CHO—C ₆ H ₃	H	C ₁₇ H ₁₃ NO ₅ S	343.36	59.53 59.71	3.82 3.68	4.08 4.21	9.34 9.07	51	127—128 Acetone—ether (1 : 1)
VIII	2-CH ₃ O-4-CHO—C ₆ H ₃	Cl	C ₁₇ H ₁₂ ClNO ₅ S	377.90	54.01 54.23	3.19 3.08	3.66 3.79	8.48 8.22	59	162—165 Acetone
IX	2-CH ₃ O-4- CH ₂ CH=CH ₂ —C ₆ H ₃	H	C ₁₉ H ₁₇ NO ₄ S	355.41	64.28 64.40	4.82 4.75	3.94 3.79	9.03 8.74	63	66—69 Ether
X	2-CH ₃ O-4- CH ₂ CH=CH ₂ —C ₆ H ₃	Cl	C ₁₉ H ₁₆ ClNO ₄ S	389.16	58.66 58.82	4.14 4.01	3.60 3.71	8.24 8.05	59	86—88 Ether
XI	3,5-(CH ₃ O) ₂ —C ₆ H ₃	H	C ₁₇ H ₁₅ NO ₅ S	345.37	59.18 59.02	4.38 4.23	4.05 4.13	9.29 9.16	70	172—173 Acetone—ether (3 : 1)
XII	2,6-(CH ₃ O) ₂ —C ₆ H ₃	H	C ₁₇ H ₁₅ NO ₅ S	345.37	59.18 59.34	4.38 4.26	4.05 3.87	9.29 9.45	61	136—138 Ether—acetone (2 : 1)
XIII	4-CH ₃ CO—C ₆ H ₄	H	C ₁₇ H ₁₃ NO ₄ S	327.36	62.44 62.27	4.00 3.89	4.28 4.19	9.80 9.73	87	136—138 Acetone—ether (3 : 1)
XIV	4-C ₆ H ₅ —C ₆ H ₄	H	C ₂₁ H ₁₅ NO ₃ S	361.42	67.10 67.31	4.18 4.09	3.87 3.74	8.88 8.58	83	190—192 Acetone—DMF (3 : 1)
XV	cyclo-C ₅ H ₉	H	C ₁₄ H ₁₅ NO ₃ S	277.34	60.70 60.84	5.45 5.32	5.05 4.87	11.57 11.22	68	108—109 Ether
XVI	cyclo-C ₅ H ₉	Cl	C ₁₄ H ₁₄ ClNO ₃ S	311.78	50.69 50.51	4.52 4.39	4.48 4.60	10.27 10.15	62	71—74 Ether
XVII	cyclo-C ₆ H ₁₁	H	C ₁₅ H ₁₇ NO ₃ S	291.28	61.91 62.12	5.88 5.70	4.81 4.87	11.01 10.95	74	103—104 Acetone—ether (1 : 2)
XVIII	cyclo-C ₆ H ₁₁	Cl	C ₁₅ H ₁₆ ClNO ₃ S	325.81	55.26 55.41	4.94 4.92	4.29 4.16	9.83 10.08	70	70—71 Acetone—ether (1 : 2)
XIX	Furyl	H	C ₁₄ H ₁₁ NO ₄ S	289.18	58.18 58.29	3.83 3.76	4.84 4.94	11.09 10.86	57	104—106 Acetone—ether (2 : 1)
XX	Furyl	Cl	C ₁₄ H ₁₀ ClNO ₄ S	323.75	51.90 51.77	3.11 3.20	4.32 4.21	9.89 9.90	61	79—82 Ether—acetone (2 : 1)
XXI	α -Naphthyl	H	C ₁₉ H ₁₃ NO ₃ S	335.38	68.12 68.30	3.91 3.79	4.18 4.07	9.57 9.66	87	159—161 Acetone—ether (1 : 1)
XXII	α -Naphthyl	Cl	C ₁₉ H ₁₂ ClNO ₃ S	369.82	61.68 61.47	3.26 3.33	3.78 3.91	8.66 8.34	80	175—177 Acetone—n-hexane (3 : 1)
XXIII	β -Naphthyl	H	C ₁₉ H ₁₃ NO ₃ S	335.38	68.12 68.28	3.91 4.11	4.18 4.07	9.57 9.47	92	156—159 Acetone—ether (1 : 1)
XXIV	β -Naphthyl	Cl	C ₁₉ H ₁₂ ClNO ₃ S	369.82	61.68 61.82	3.26 3.15	3.78 3.86	8.66 8.57	88	147—150 Acetone—ether (1 : 1)
XXV	8-Quinolyl	H	C ₁₈ H ₁₂ N ₂ O ₃ S	336.37	64.31 64.50	3.59 3.42	8.33 8.25	9.54 9.45	67	163—166 Acetone—DMF (4 : 1)
XXVI	8-Quinolyl	Cl	C ₁₈ H ₁₁ ClN ₂ O ₃ S	370.81	58.43 58.57	2.99 3.11	7.57 7.44	8.66 8.73	64	167—169 Acetone—DMF (4 : 1)

almost halved (25.14 %). The presence of acetyl group in the position 4 (XIII) did not mean any change in comparison with 3 phenoxy carbonylmethyl-2-benzothiazolinone with 32.71 % activity [1]. The influence

of the moiety other than phenyl has been studied in the rest of the series. The introduction of biphenyloxy group (XIV) caused a loss of the stimulation effect. Cyclopentyl, in the case of XV, contributed to

Table 2. IR and UV Spectral Data of the Synthesized Compounds

Compound	$\tilde{\nu}(\nu(\text{C}=\text{O}))/\text{cm}^{-1}$		$\lambda_{\text{max}}/\text{nm}$ ($\log(\epsilon/(\text{m}^2 \text{mol}^{-1}))$)	
I	1678, 1757	216 (3.46)	282 (2.40)	288 (2.36)
II	1682, 1756	218 (2.97)	284 (1.89)	292 (1.88)
III	1678, 1755	216 (3.52)	282 (2.42)	288 (2.41)
IV	1683, 1755	228 (3.31)	284 (2.30)	292 (2.33)
V	1678, 1781, 1687*	216 (3.34)	282 (2.39)	288 (2.29)
VI	1677, 1777, 1748*	216 (3.49)	280 (2.52)	290 (2.40)
VII	1687, 1786, 1701*, 1769*	222 (3.49)	282 (2.67)	288 (2.73)
VIII	1687, 1786, 1701*, 1769*	224 (3.54)	252 (3.11)	294 (2.64)
IX	1678, 1782, 1766*	216 (3.54)	280 (2.76)	290 (2.53)
X	1680, 1778	222 (3.58)	280 (2.56)	293 (2.35)
XI	1677, 1783, 1768*	214 (3.14)	278 (2.07)	288 (1.96)
XII	1678, 1778	216 (3.46)	280 (2.45)	288 (2.34)
XIII	1681, 1783, 1766*	212 (3.60)	280 (2.60)	290 (2.45)
XIV	1677, 1715, 1784, 1690*	216 (3.40)	280 (2.65)	290 (2.33)
XV	1676, 1744, 1685*	216 (3.33)	282 (2.40)	288 (2.39)
XVI	1681, 1743	212 (3.36)	280 (2.42)	290 (2.15)
XVII	1677, 1738, 1687*, 1755*	218 (3.33)	282 (2.43)	288 (2.42)
XVIII	1682, 1741	222 (3.54)	286 (2.31)	294 (2.34)
XIX	1678, 1757	216 (3.52)	282 (2.38)	288 (2.37)
XX	1682, 1756	224 (3.55)	284 (2.29)	294 (2.32)
XXI	1678, 1776, 1762*	226 (3.34)	280 (2.99)	
XXII	1681, 1776	222 (3.70)	280 (2.71)	292 (2.60)
XXIII	1678, 1774, 1759*	224 (3.68)	276 (2.83)	288 (2.71)
XXIV	1681, 1773	222 (3.65)	274 (2.49)	284 (2.44)
XXV	1677, 1783, 1764*	226 (3.46)	288 (2.79)	314 (2.36)
XXVI	1682, 1778	222 (3.16)	292 (2.19)	314 (1.88)

*The band observed as a "shoulder" of another band.

Table 3. Growth Regulation Activity of the Synthesized Compounds Tested on *Triticum aestivum* L.

Compound	Stimulation ($c = 10^{-5} \text{ mol dm}^{-3}$)		Compound	Stimulation ($c = 10^{-5} \text{ mol dm}^{-3}$)	
	Δ/mm	$\Delta/\%$		Δ/mm	$\Delta/\%$
I	1.38	15.41*	XV	2.04	35.11*
II	1.03	22.63*	XVI	0.26	5.53
III	1.72	33.14*	XVII	1.27	23.73*
IV	-0.08	-1.43	XVIII	0.66	12.33
V	-0.32	-5.51	XIX	1.04	20.03*
VI	0.37	6.36	XX	2.55	47.66*
VII	1.00	12.44	XXI	-0.07	-1.26
VIII	1.40	28.28*	XXII	0.21	4.61
IX	2.24	44.35*	XXIII	1.07	20.00*
X	1.95	39.39*	XXIV	2.29	42.80*
XI	2.02	40.00*	XXV	1.94	36.88*
XII	1.27	25.14*	XXVI	1.09	20.72*
XIII	1.62	32.07*	IAA	5.93	100.33
XIV	0.30	7.33	2,4-D	2.56	51.09

*Highly significant activity.

a relatively high activity (35.11 %) but chlorine in the position 4 (XVI) caused an actual ineffectiveness. The derivatives containing cyclohexyl chain (XVII, XVIII) did not exhibit significant activity changes. The introduction of the furyloxy group (XIX, XX) improved the stimulation effect, above all, in the compound XX with chlorine in the position 4, providing thus the highest observed stimulation activity among synthesized compounds (47.66 %). Interesting results have been obtained for naphthyl esters. While the α -naphthyl derivatives (XXI, XXII) are ineffective, the

β -naphthyl derivatives show activity of high significance. High values have also been recorded for 8-quinolyl compounds (XXV, XXVI).

The influence of chlorine in the position 4, and that of the geometry of a molecule on its stimulation activity, will be subjected to further study.

EXPERIMENTAL

The characterization of the synthesized compounds is given in Table 1. UV spectra were measured using

methanolic solutions ($c = 10^{-4}$ mol dm $^{-3}$) in 1 cm thick cuvette on HP 8452 A spectrophotometer. The position of the absorption maxima was determined from the fourth derivation of the spectra. IR spectra were measured on PE 180 apparatus in NaCl cuvettes of 0.1 mm thickness, the compounds being dissolved in CHCl $_3$. The spectra were corrected for polystyrene absorption. The growth regulation tests were performed on the coleoptile growth of wheat (*Triticum aestivum* L.) and the results were compared to those obtained with the standards — 3-indolylacetic acid (IAA) and (2,4-dichlorophenoxy)-acetic acid (2,4-D) in the concentration of 10^{-5} mol dm $^{-3}$ according to the used method [4].

3,4-Disubstituted 2-Benzothiazolinones

To 20 cm 3 of dry acetone, the following materials were added consecutively: (2-oxobenzothiazolin-3-yl)acetyl chloride or its 4-chloro derivative (0.01 mol),

pyridine (0.79 g; 0.01 mol) and 2- or 4-chlorobenzyl alcohol, resp. derivatives of phenol, cyclopentanol, cyclohexanol, furyl alcohol, α - and β -naphthol, and 8-hydroxyquinoline (0.01 mol). The reaction mixture was then heated to reflux for 3 h and then it was poured into 80–100 cm 3 of cold water. The solid portion was filtered off and crystallized after drying from the solvent mixture.

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