

## 2-(4*H*-4-Oxo-benzopyran-3-yl)benzothiazolium Salts

[C021]

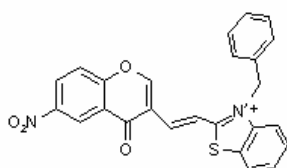
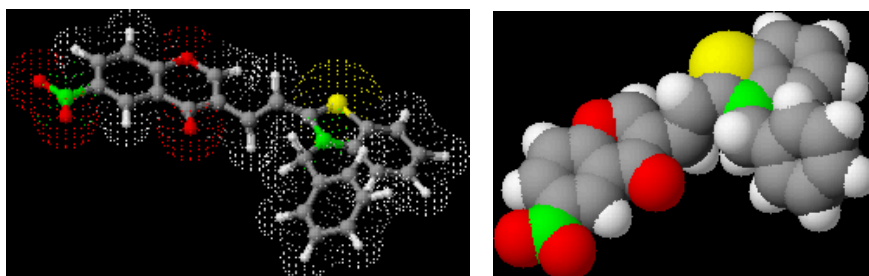
### Synthesis, Reactions and Plant Growth Activity

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**Abstract:** One-pot and facile preparation of novel 2-(4*H*-4-oxo-benzopyran-3-yl)benzothiazolium salts **3** is described using the fast condensation of 3-formylchromones **1** with 3-benzyl-2-methylbenzothiazolium (or benzoxazolium) bromides **2**. Reactions under microwave irradiation, in comparison with classical reactions, proceeded significantly faster and with high yields. Reaction of benzothiazolium salts with secondary and primary amines was also studied. Synthesized chromone derivatives stimulated significantly the growth of the radicle and the hypocotyl at concentrations of 0.1 and 1 ppm, respectively.

**Keywords:** Chromones, Benzoxazolium Salts, Microwave synthesis, Aldol Reactions, 3-Formylchromones, Plant Growth Activity

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### Introduction

This work is aimed at the preparation of chromones **3** with strong electron withdrawing benzothiazolium or benzoxazolium groups at C-3 position of chromone ring. Generally, C-3 modified chromones are useful reactive agents. They are good acceptors of nucleophiles and they can rearrange

under mild conditions<sup>1-4</sup>. It is obvious these azole salts have versatile synthetic utility in the field of new heterocycles.

In our previous papers the condensations of 3-formyl-chromones **1** with various heterocyclic components with active methyl- or methylene- groups as creatinine<sup>5</sup>, rhodanine<sup>5</sup>, benzothiazoles<sup>6</sup>, furopyroles<sup>7</sup>, butanolides<sup>8</sup> were described. The photochemical behavior, photochromism and thermochromism of chromone derivatives of carboxyimide were studied by UV and fluorescent spectral methods<sup>9</sup>. The activity of similar chromone salts on photosynthetic electron transport in spinach chloroplast was also reported<sup>10,11</sup>.

The main goal of this work was a synthetic study of chromone salts **3** and **4** by classical and microwave-irradiation methods, respectively, and kinetic and theoretical study of sensitivity of these derivatives to various nucleophiles.

## Results and Discussion

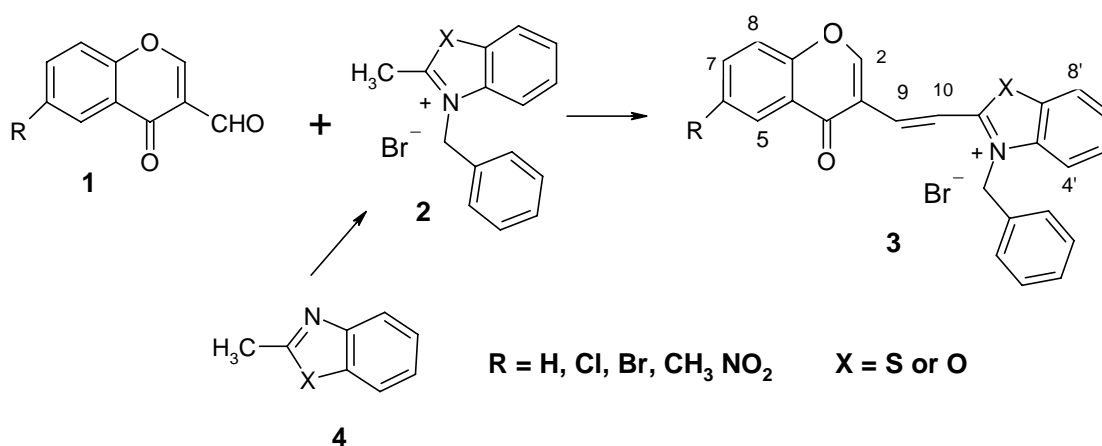
In this article we report the fast, facile and one-pot synthesis of 2-[(4*H*-4-oxobenzopyran-3-yl)ethenyl]benzothiazolium (or benzoxazolium) salts **3** by condensation of three starting compounds: 3-formylchromones **1**, 2-methylbenzothiazole **4** and benzylbromide in certain solvents: CH<sub>3</sub>NO<sub>2</sub>, CH<sub>3</sub>CN, CHCl<sub>3</sub> and (CH<sub>3</sub>CO)<sub>2</sub>O. Our experimental results showed that N-substituted 2-methylbenzothiazolium salt **2** as the starting material was more efficient component for the condensation than 2-methylbenzoxazoles **4** in the classical and also in the microwave - assisted aldol synthesis.

The microwave irradiation of the reaction mixture for 8 - 10 min gave yields of product about 10 - 30 % higher with better purity in comparison with classical conditions (3 - 4 hours, 90 - 100 °C). The products **3** are solids of pale yellow color, rather insoluble in common solvents, with high melting points. They are air-moisture sensitive and rapidly can change their color to red, violet or brown.

2-(4*H*-4-Oxobenzopyran-3-yl)benzothiazolium salts **3** readily reacted with nucleophiles under mild conditions. The <sup>1</sup>H-NMR spectra of prepared compounds confirmed the proposed structure. The signals of protons displayed chemical shifts and multiplicities corresponding to their surroundings. The <sup>1</sup>H-NMR spectra showed a well distinguishable intensive singlet signal at δ = 9.4 – 9.6 ppm for proton at C-2 position and singlet signals for methylene group at 6.15 ppm. Both these signals are characteristic for chromone system protons if the chromone ring is substituted by strong electron withdrawing group at 3-position.

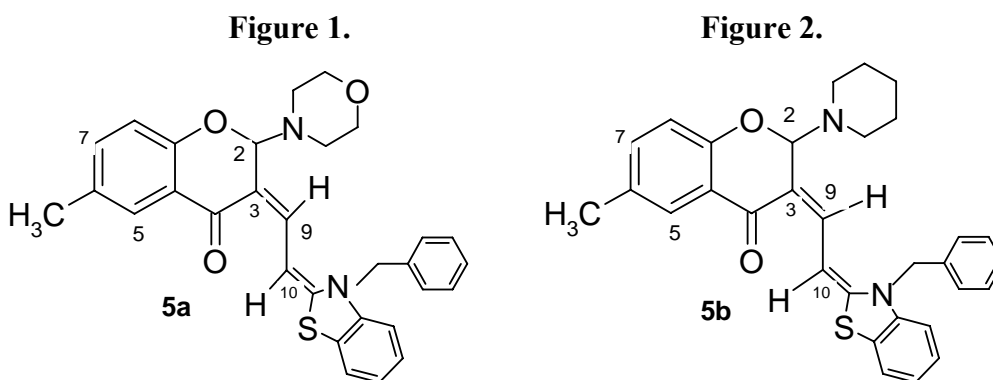
Stereochemistry of the salts **3** at their olefinic double bond is *trans*, as is evident from the signals and coupling constants. Signals of H-9 proton occurred at δ = 8.3 – 9.0 ppm and for H-10 at δ = 8.0 – 8.2 ppm. Both signals occurred as doublets with the coupling constants of 15.5 Hz.

Scheme 1.

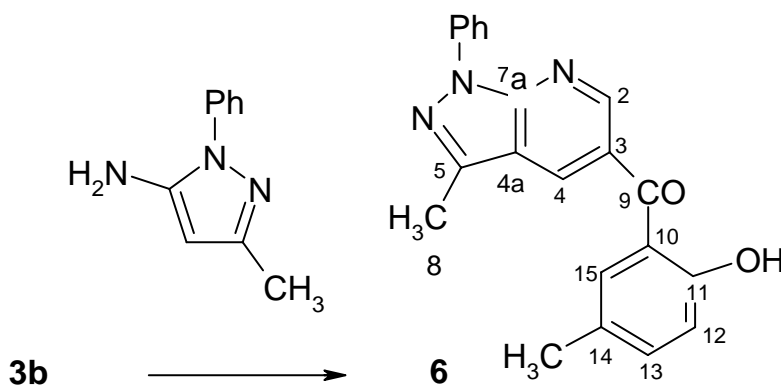


Reaction of prepared salts **3** with secondary amines (morpholine and piperidine) showed that nucleophilic attack is realized on the C-2 site of chromone ring without opening of pyrone system. Morpholine and piperidine underwent 1,4-addition to chromone salts **3** and formed products **5a** and **5b**, respectively. This is in agreement with the similar 1,4-addition of piperidine already described on chromone-3-carboxylic acids by Ghosh<sup>12</sup>. <sup>1</sup>H NMR spectra of compounds **5a** and **5b** had no occurrence of signal for phenolic OH-group (Figure 1. and 2.). From the comparison of chromone and benzothiazole <sup>1</sup>H NMR spectra signals of **3** with the corresponding signals of **5a** and **5b** are evident the reasonable changes in the structure of both **5a** and **5b** caused by the absence of positive charge in the structure of **5a** and **5b** ( **Table 2.** and **Table 3.**).

Compound **6** was prepared by treatment of the benzothiazole salts **3** with selected primary amine 5-amino-3-methyl-1-phenylpyrazole. In this reaction the salts **3** undergo a spontaneous degradation. The benzothiazolium part of **3** is split of and then the intermediate continues to stabilize the molecule **6** by two key steps; the first step includes process of electrophilic substitution on pyrazole ring and the second cyclisation step results into pyridin cycle. We already isolated the same product from reaction of 6-methyl-3-formylchromone with 5-amino-3-methyl-1-phenylpyrazole in ethanol and p-toluensulfonic acid as catalyst.<sup>13</sup> (**Scheme 2.**).



**Scheme 2.**



## Experimental part

Melting points (uncorrected) of the synthesized compounds were determined on the Kofler block. The microanalyses (Carlo Erba Instrumentazione 1106) were in satisfactory agreement with the calculated values (the results for C, H, and N showed an agreement within  $\pm 0.40\%$ ). The respective data are summarized in Tables 1-3. Microwave assisted reactions were carried out in a Lavis-1000 MultiQuant microwave oven. The apparatus was adapted for laboratory application with magnetic stirring and an external reflux condenser. <sup>1</sup>H-NMR spectra were measured at 300MHz, <sup>13</sup>C-NMR spectra at 75MHz on a Varian Gemini 2000 NMR spectrometer. For some compounds, TESLA BS487

(80MHz) instrument was used using saturated solutions of the compounds in CF<sub>3</sub>COOH-d. Chemical shifts are given in  $\delta$ -scale, coupling constants in Hz, TMS was used as an internal standard.

The 3-formylchromones **1** were prepared by Vilsmeier double formylation of appropriate 2-hydroxyacetophenones<sup>14</sup>. The preparation of benzothiazolium salts by classical procedures was carried out as described in detail elsewhere<sup>6</sup>.

### 3-Benzyl-2-methylbenzothiazolium bromide **4**

A stirred mixture of 2-methylbenzothiazole (0.5 g, 3.35 mmol) and benzylbromide (0.573 g, 3.35 mmol) in anhydrous nitromethane (2 ml), or acetonitrile (2 ml) was irradiated for 20 minutes at 270 W in microwave oven. Pale-green precipitate was diluted by acetone, filtered off and dried. Yields were about 55 % (acetonitrile) or 70 % (nitromethane), m.p. 241 - 243 °C. The product was identical to that prepared by classical method<sup>5,6</sup> as evidenced by <sup>1</sup>H NMR.

### 3-Benzyl-2-[(6-R-chromon-3-yl)ethenyl]benzothiazolium bromides **3**

#### *Method A (by irradiation).*

A stirred mixture of 3-benzyl-2-methylbenzothiazolium bromide **2** (1 mmol) and 3-formylchromone derivative **1** (1 mmol) in 2 ml of anhydrous nitromethane was irradiated at 270 W for 2-8 minutes. Solid products were filtered off, washed with warm acetone and crystallized from acetonitrile.

#### *Method B (one - pot - reaction, by irradiation).*

A stirred mixture of benzylbromide (1 mmol), 2-methylbenzothiazole **4** (1 mmol) and appropriate 3-formylchromone derivative **1** (1 mmol) in anhydrous nitromethane (2 ml) was irradiated at 270 W for 2-8 minutes. The isolation of products was analogous as in *method A*. Yields were in the range of 84-89%.

#### *Method C (classical reaction).*

The reaction mixture analogous as in *method A* was refluxed for 6 hours under argon atmosphere. Then the crystals were filtered off and recrystallized from acetonitrile. Yields were about 50-60 %. Benzoxazole derivative **3g** was also prepared by the *method B*.

### Preparation of compound **5a**, **5b** and **6** - aminolysis of salts **3**

The mixture of 3-benzyl-2-(6-CH<sub>3</sub>-chromon-3-yl)ethenylbenzothiazolium bromide **3b** (1 mmol) and morpholine or piperidine (2 mmol) was refluxed in ethanol (20 ml) for 1 hour. Then the reaction mixture was cooled, the red crystals (compounds **5a**, **5b**) or yellow crystals (compounds **6**) were filtered off and washed with warm ethanol. The yields of compounds were about 60 - 70 %.

**Table 1.**  
Reaction time, yields and melting points of chromones **3a** - **\*3g**  
(microwave irradiation, \*benzoxazole derivative)

compounds	<b>3a</b>	<b>3b</b>	<b>3c</b>	<b>3d</b>	<b>3e</b>	<b>3f</b>	<b>*3g</b>
reaction time [min.]	10	8	6	7	4.5	6	2.5
yields [%]	75.9	68.2	76	81	81	79	54
melting point °[C]	215-217	171-173	242-245	253-256	294-297	255-258	221-223

Table 2.

Analytical characteristics of chromones 3

(\*benzoxazole derivative, \*\* measured in CF<sub>3</sub>COOH-d, 80 MHz)

Comp.	Formula M <sub>r</sub>	Elemental analysis (calc. / found)					
		%C	%H	%N	%S	%Br	
<b><sup>1</sup>H NMR, δ (ppm), DMSO-d<sub>6</sub>, 300 MHz, 100°C</b>							
<b>3-Benzyl-2-[(6-R-4H-4-Oxo-benzopyran-3-yl)ethenyl]benzothiazolium bromides</b>							
<b>3a</b>	H	C <sub>25</sub> H <sub>18</sub> BrNO <sub>2</sub> S	63.03	3.81	2.94	6.73	16.77
		476.4	63.21	3.86	2.82	6.35	17.06
6.15s <sub>2</sub> ( 2H, CH <sub>2</sub> ); 7.39s <sub>2</sub> ( 5H, Ph); 7.71t <sub>2</sub> ( 1H, <sup>3</sup> J=7.97Hz, <sup>3</sup> J=7.14Hz, H-8); 7.77d <sub>2</sub> ( 1H, <sup>3</sup> J=8.24Hz, H-11); 7.81-7.89 m <sub>2</sub> (3H,H-5,6,7); 8.11d ( 1H, <sup>3</sup> J=15.66Hz, H-10); 8.21d <sub>2</sub> ( 1H, <sup>3</sup> J=7.69Hz, H-13); 8.31d ( 1H, <sup>3</sup> J=8.24Hz, H-12); 8.59d <sub>2</sub> ( 1H, <sup>3</sup> J=7.69Hz, H-14); 8.69d ( 1H, <sup>3</sup> J=15.66Hz, H-9); 9.17 s (1H, H-2)							
<b>3b</b>	CH <sub>3</sub>	C <sub>26</sub> H <sub>20</sub> BrNO <sub>2</sub> S	63.89	4.11	2.86	6.54	16.30
		490.4	63.68	4.32	2.73	6.38	16.58
2.47 (s, 3H, CH <sub>3</sub> ); 6.15 (s, 2H, CH <sub>2</sub> ); 7.40 s <sub>2</sub> (5H, Ph); 7.71-7.72m <sub>2</sub> ( 2H, H-8,11); 7.8-7.89m <sub>2</sub> ( 2H, H-7,14); ;7.96 d ( <sup>4</sup> J=1.7Hz, H-5); 8.07d ( 1H, <sup>3</sup> J=15.4Hz, H-10); 8.35d ( 1H, <sup>3</sup> J=9.8Hz, H-12); 8.52d (1H, <sup>3</sup> J=10Hz, H-11); 8.70d ( 1H, <sup>3</sup> J=15.4Hz, H-9); 9.18s <sub>2</sub> ( 1H, <sup>3</sup> J=15.38 Hz, H-10)							
<b>3c**</b>	Cl	C <sub>25</sub> H <sub>17</sub> BrClNO <sub>2</sub> S	58.78	3.35	2.74	6.28	15.64
		510.8	58.25	3.42	2.61	6.06	15.21
6.11 s (2H, CH <sub>2</sub> ); 7.307-7.505 m (5H, Ph); 7.761-8.326 m (8H, H-5,7,8,10 -14); 8.744 s (1H, H-10); 9.008 d ( <sup>3</sup> J=15.38 Hz, 1H, H-9)							
<b>3d</b>	Br	C <sub>25</sub> H <sub>17</sub> Br <sub>2</sub> NO <sub>2</sub> S	54.08	3.09	2.52	5.77	28.78
		555.3	53.84	3.12	2.47	5.68	29.12
6.16 s (2H, CH <sub>2</sub> ); 7.37-7.41 m (5H, Ph); 7.79-7.88 m (3H, H-8,11,12); 8.01dd (1H, <sup>3</sup> J=7.2Hz, <sup>4</sup> J=2.Hz, H-7); 8.06 d (1H, <sup>3</sup> J=15.6Hz, H-10); 8.24 d (1H, <sup>4</sup> J=1.9Hz, H-5); 8.34 d ( 1H, <sup>3</sup> J=8Hz, H-13); 8.52 d (1H, <sup>3</sup> J=8Hz, H-14); 8.66 d (1H, <sup>3</sup> J=15.5Hz, H-9); 9.21 s <sub>2</sub> ( 1H, H-2)							
<b>3e</b>	NO <sub>2</sub>	C <sub>25</sub> H <sub>17</sub> BrN <sub>2</sub> O <sub>4</sub> S	57.59	3.28	5.37	6.15	15.33
		521.4	57.32	3.35	5.14	5.95	14.82
6.21s (2H, CH <sub>2</sub> ); 7.33-7.46 m (5H, Ph); 7.79-7.92 m (2H, H-12,13); 8.05 d (1H, <sup>3</sup> J=9.15Hz, H-8); 8.11 d (1H, <sup>3</sup> J=.15Hz, H-9); 8.37d (1H, <sup>3</sup> J=8.24Hz, H-11); 8.59 d ( 1H, <sup>3</sup> J=8.55Hz, H-14); 8.63 dd (1H, <sup>3</sup> J=9.15Hz, <sup>4</sup> J= 2.9Hz,H-7); 8.74 d (1H, <sup>3</sup> J=.15Hz, H-10); 8.8 d (1H, <sup>4</sup> J=.2.9Hz, H-5); 9.36 s (1H, H-2)							
<b>3f</b>	6-CH <sub>3</sub> 8-Cl	C <sub>26</sub> H <sub>19</sub> BrClNO <sub>2</sub> S	59.50	3.65	2.67	6.11	15.22
		524.8	59.30	3.57	2.76	5.89	15.84
2.46 s (3H, CH <sub>3</sub> ); 6.16 s (2H, CH <sub>2</sub> ); 7.39 s (5H, Ph); 7.83-7.92 m (4H, H-5,7,11,12); 8.08d (1H, <sup>3</sup> J=15.7Hz, H-10); 8.36 d (1H, <sup>3</sup> J=8.6Hz, H-13); 8.52 d (1H, <sup>3</sup> J=8.7Hz, H-14); 8.7 d (1H, <sup>3</sup> J=15.7Hz, H-9); 9.29 s ( 1H, H-2)							
<b>*3g</b>	H	C <sub>25</sub> H <sub>18</sub> BrNO <sub>3</sub>	65.23	3.94	3.04		17.36
		460.3	64.94	3.82	3.04		17.56
5.98m s (2H, CH <sub>2</sub> ); 7.36-7.86 m (5H, H-15 - 19); 7.73-7.86 m (4H, H-6,8,12,13); 7.89-7.97 m (1H, H-7); 8.06 d (1H, <sup>3</sup> J 7.42Hz, H-14 ); 8.14 d (1H, <sup>3</sup> J= 7.44Hz, H-11 ); 8.22 dd (1H, <sup>3</sup> J =7.92Hz, <sup>4</sup> J=1.65Hz,H-5 ); 8.33 d (1H, <sup>3</sup> J=15.65Hz, H-10); 8.52d <sub>2</sub> (1H, <sup>3</sup> J =15.68Hz, H-9); 9.29 s 1H, H-2)							

**Table 3.**Analytical characteristics of compounds 5 and 6 (NMR-spectra in CDCl<sub>3</sub>, δ(ppm))

<b>3-benzyl-2-(2-(1-morpholinyl)-chromon-3-yl)ethenylbenzothiazole (5a)</b>		
C <sub>30</sub> H <sub>28</sub> N <sub>2</sub> O <sub>3</sub> S 496.6	161-162 °C	Calc.: 72.55 %C; 5.66 %H; 5.64%N; 6.45%S Found:72.39 %C; 5.46 %H; 5.55%N; 6.55% S
<sup>1</sup> H NMR: 2.29 s (3H, CH <sub>3</sub> ); 2.4 –2.8 m (4H, CH <sub>2</sub> ); 3.2 –3.4,m (4H, CH <sub>2</sub> ); 5.13 s (2H, CH <sub>2</sub> ); 5.64 s (1H, H-2); 5.86 d (1H, <sup>3</sup> J=12.3Hz, H-9); 6.89 d (1H, <sup>3</sup> J=8.24, H-8) 7.72 d ( <sup>4</sup> J=1.6Hz, H-5); 7.10-7.23 m (5H, Ph); 7.30-7.41 m (4H, Ph-Bt) 7.49 d, (1H, <sup>3</sup> J=12.2Hz, H-10);.		
<b>3-benzyl-2-(2-(1-piperidyl)-chromon-3-yl)ethenylbenzothiazole (5b)</b>		
C <sub>31</sub> H <sub>30</sub> N <sub>2</sub> O <sub>2</sub> S 494.6	182-184 °C	Calc.: 75.27 %C; 6.11%H; 5.66%N; 5.48%S Found: 75.39 %C; 5.98%H; 5.68%N; 5.37%S
<sup>1</sup> H NMR: 1.72-1.78 m (2H, CH <sub>2</sub> ); 1.5-1.6 m (4H, CH <sub>2</sub> ); 2.29 s, (3H, CH <sub>3</sub> ); 2.37 –2.49 m (4H, CH <sub>2</sub> ); 5.13 s(2H, CH <sub>2</sub> ); 5.64 s (1H, H-2); 5.92 d (1H, <sup>3</sup> J=12.4Hz, H-9); 6.77 d (1H, <sup>3</sup> J=8.24, H-8); 7.45 d (1H, <sup>3</sup> J=12.4Hz, H-10);. 7.72 d ( <sup>4</sup> J=1.6Hz, H-5); 7.10-7.23 m (5H, Ph); 7.3-7.38 m (4HPh-Bt)		
<b>3-(2-hydroxy-5-methylbenzoyl)-5-methyl-7-phenylpyrazolo[3,4-<i>b</i>]pyridine(6)</b>		
C <sub>21</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> 343.4	142-144 °C	Calc.: 73.38 %C; 4.99 %H; 12.23%N Found: 73.22 %C; 4.84 %H; 12.27 %N
<sup>1</sup> H NMR: 2.28 s (3H, H-7'); 2.72 s (3H, H-8); 7.04 d (1H, J(3',4')=7.7Hz, H-3'); 7.34 tt 1H, (J(11,12)=7.6Hz, J(10,12)=1.1Hz, H-12); 7.38 dd, 1H, J(3',4')=7.7, J(4',6')=0.8(H-4'); 7.39 d (1H, J(4',6')=0.8Hz); 7.55 t (2H, J(10,11)=7.6Hz, H-11); 8.26 dd (2H, J(10,11)=7.6Hz, J(10,12)=1.1Hz, H-10); 8.47d, 1H, J(5,7)=1.9(H-7); 8.94 d (1H, J(5,7)=1.9Hz, H-5). <sup>13</sup> C NMR:12.72(C-8); 20.73(C-7'); 116.70(C-3a); 118.74(C-3'); 119.31(C-1'); 121.48(C-10); 126.54(C-12); 127.76(C-6); 128.45(C-5'); 129.41(C-11); 131.82(C-7); 132.88(C-6'); 137.93(C-4'); 139.25(C-9); 144.48(C-3); 150.23(C-5); 151.51(C-3b); 161.37(C-2'); 199.04(C-15).		

## Biological Part

### Introduction

Many derivatives of benzothiazole were tested for a different biological activity<sup>10,11</sup> and also examined for their plant growth regulating properties. They may stimulated the plant regeneration, activity of peroxidases, the prolongation of growth and may induce also the dedifferentiation and morphogenesis in *in vitro* conditions<sup>15,16</sup>. 3-R-substituted benzotiazole derivatives acted on the physiological and biochemical processes in many agricultural crops<sup>17</sup>.

### Material and Methods

The **stock solutions** of chromone-benzotiazole salts **3** were prepared in dimethylsulfoxid (DMSO). The final concentration of DMSO in all biological experiments, including the control, was held constant at 1 % by volume. This concentration of DMSO had no detectable effect on the growth plants under experimental conditions.

For determination of **stimulated growth activity** like indoleacetic acid (IAA) we used the bioassay as described by Merrill<sup>18</sup> in this modification: Twenty seeds of cucumber (*Cucumis sativus* L. cv. Regina) were placed in 12 cm Petri-dishes on two layers of filter paper Whatman № 2. The filter paper was wetted with 15 ml of distilled water (control), or the indicated benzothiazole solution at 0.1, 1 and 10 ppm concentration. The Petri-dishes were placed to a dark box and incubated at 28 °C. After

7 days the seedlings were taken out and length of the radicle and hypocotyl were measured to the nearest millimeter. The stimulated effect was evaluated and compared with the  $\beta$ -indoleacetic acid (IAA) control at 0.001, 0.01, 0.1, 1 and 10 ppm concentrations.

For **corn bioassay** in nutrient culture the seeds of corn (*Zea mays* L. cv. Greta) were pregerminated by soaking them in water for 24 hours. Twenty-five seeds were placed on wet filter paper in the Petri-dishes of 20 cm diameter for 48 hours at 25 °C to the dark box. Seeds selected for treatment had a coleoptile emergence of 10 to 15 mm.

For determination of **retardant activity** like abscissic acid (ABA) we used the seedlings bioassay as described by Dathe<sup>19</sup> in this modification: Twenty seedlings were chosen per every variant and placed after two seedling in glass flasks containing 4 ml of half nutrient solution prepared according Brown and Dalton<sup>20</sup> with application of testing compounds in 1, 10 and 100 ppm concentrations. The treated and untreated corn plants were cultivated under glass cover in climatic box (temperature 25/15 °C during 16 hours photo period and light intensity of 60  $\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  with a relative humidity of 80 %). The level of the solutions in the flasks was maintained daily by carefully adding nutrient solution through the glass tubing by means of an automatic syringe. The length of the corn shoots was measured after 7 days and compared with the control and standard ABA.

The trials were made in **triplicate** and dates are presented as arithmetic averages of the individual experiments. Bioassay results were statistically evaluated using the **Student's t-test**.

## Results and Discussion

The effects of benzothiazole derivatives were tested on the germination and early growth of cucumber and corn seedlings. Derivatives inhibited germination over 100 ppm concentration and inhibited growth of cucumber radicle and hypocotyl at the range of 1-10 ppm concentrations.

Compounds **3a**, **3d** and **3i** have no retard effect on hypocotyl but on the radicle all compounds except of compound **3i** have inhibitory effect (**Table 4**). The prepared derivatives stimulated significantly the radicle and hypocotyl growth at lower concentrations of 0.1 and 1 ppm. It is obvious from our experimental data that the biological growth effects depend on concentrations of tested compounds. In general, the inhibition activity was observed at higher, and the stimulation activity at lower concentrations (**Table 4**. and **Table 5**).

The most effective benzothiazole derivative with stimulating activity on **cucumber seedlings** was compound **3a**, the best retardant was compound **3h** (**Table 4**. and **Table 5**).

The compound with the highest retardant activity on **corn seedlings** was the same compound **3h** at 100 ppm concentration (**Table 5**).

The **enhancement of growth** of cucumber and corn plant seedlings **at the low concentrations** and, on the other hand, their **inhibition effect at higher concentrations** observed in benzothiazole derivatives are according to Merrille's<sup>18</sup> **characteristic growth pattern for auxins**. Indolebutyric acid (IBA) and naphthyl acetic acid (NAA) were found to increase root development in the propagation of stem cuttings in many plant species.

According to our opinion the compounds which stimulates both root and shoot growth of plants, as benzothiazole derivatives at lower rates do, can be used in higher concentration for herbicidal purposes, such as preparation picloram (pyridine- $\alpha$ -carboxylic acid) which is know as an auxine-type herbicide<sup>21</sup>.

Table 4.

Effects of the benzothiazole derivatives 3a –3h  
on cucumber *Cucumis sativus* L. cv. *Regina* seedlings

Compounds R	Concentrations (ppm)	Mean length (mm)		% of control	
		Radicle	Hypocotyl	Radicle	Hypocotyl
Control	—	63.5	36.6	100.0	100.0
3b	0.1	59.0	44.7	92.9	122.1 <sup>a</sup>
	1.0	52.2	38.2	82.2 <sup>a</sup>	104.4
	10.0	40.0	26.2	63.0 <sup>a</sup>	71.6 <sup>a</sup>
6-CH <sub>3</sub>	0.1	89.7	49.2	141.2 <sup>a</sup>	134.4 <sup>a</sup>
	1.0	79.7	47.5	125.5 <sup>a</sup>	129.8 <sup>a</sup>
	10.0	64.0	43.2	100.8	118.0 <sup>a</sup>
3i	0.1	80.0	50.5	126.0 <sup>a</sup>	137.9 <sup>a</sup>
	1.0	63.0	47.0	99.2	128.4 <sup>a</sup>
	10.0	61.0	10.7	96.1	111.2 <sup>b</sup>
6-Br	0.1	83.0	52.0	130.7 <sup>a</sup>	142.1 <sup>a</sup>
	1.0	77.0	48.5	121.2 <sup>a</sup>	132.5 <sup>a</sup>
	10.0	63.0	44.7	99.2	122.1 <sup>a</sup>
H	0.1	92.0	46.2	144.9 <sup>a</sup>	126.2 <sup>a</sup>
	1.0	71.8	39.8	113.1 <sup>b</sup>	108.7
	10.0	45.8	26.8	72.1 <sup>a</sup>	73.2 <sup>a</sup>
6-Cl	0.1	74.6	41.2	117.5 <sup>b</sup>	112.6 <sup>a</sup>
	1.0	70.4	35.8	110.9 <sup>b</sup>	97.8
	10.0	48.8	33.7	76.8 <sup>b</sup>	92.1
6-F	0.1	72.6	47.0	114.3 <sup>b</sup>	128.4 <sup>a</sup>
	1.0	51.8	44.2	81.6 <sup>a</sup>	120.8 <sup>a</sup>
	10.0	48.6	35.2	76.5 <sup>a</sup>	96.2
3e	0.1	61.2	38.8	96.4	106.0
	1.0	39.0	25.4	61.4 <sup>a</sup>	69.4 <sup>a</sup>
	10.0	31.2	19.2	49.1 <sup>a</sup>	52.4 <sup>a</sup>
6-NO <sub>2</sub>	0.001	104.8	58.9	165.0 <sup>a</sup>	160.9 <sup>a</sup>
	0.01	94.8	51.2	149.3 <sup>a</sup>	139.9 <sup>a</sup>
	0.1	86.4	44.6	136.1 <sup>a</sup>	121.8 <sup>a</sup>
3h	1.0	79.8	43.1	125.7 <sup>a</sup>	117.7 <sup>a</sup>
	10.0	32.2	27.9	50.7 <sup>a</sup>	76.2 <sup>a</sup>
	10.0	32.2	27.9	50.7 <sup>a</sup>	76.2 <sup>a</sup>
*6-CH <sub>3</sub>	0.001	104.8	58.9	165.0 <sup>a</sup>	160.9 <sup>a</sup>
β-indole- acetic acid (IAA) standard	0.01	94.8	51.2	149.3 <sup>a</sup>	139.9 <sup>a</sup>
	0.1	86.4	44.6	136.1 <sup>a</sup>	121.8 <sup>a</sup>
	1.0	79.8	43.1	125.7 <sup>a</sup>	117.7 <sup>a</sup>
	10.0	32.2	27.9	50.7 <sup>a</sup>	76.2 <sup>a</sup>

\*Benzoxazole derivative

Values followed by the letter **a** are significantly different at the 1 % and the ones followed by the letter **b** are significantly different at the 5 % level against the control as determined by Student's t-test.



Table 5.

Effects of the benzothiazole derivatives 3a – 3h  
on the shoot length of corn *Zea mays L. cv. Greta*

Compounds R	Concentrations (ppm)	Mean length of the shoot (mm)	% of control
Control	—	121.4	100.0
3b 6-CH <sub>3</sub>	1	113.0	93.1
	10	65.0	53.5 <sup>a</sup>
	100	45.0	37.1 <sup>a</sup>
3i 6-OH	1	132.0	108.7
	10	146.0	120.3 <sup>a</sup>
	100	143.5	118.2 <sup>a</sup>
3d 6-Br	1	125.0	102.9
	10	142.0	116.9 <sup>a</sup>
	100	93.0	76.6 <sup>a</sup>
3a H	1	155.5	128.1 <sup>a</sup>
	10	143.0	117.8 <sup>a</sup>
	100	142.0	116.9 <sup>a</sup>
3c 6-Cl	1	185.0	152.4 <sup>a</sup>
	10	141.0	116.1 <sup>a</sup>
	100	98.5	81.1 <sup>a</sup>
3j 6-F	1	114.0	93.9
	10	107.0	88.1 <sup>b</sup>
	100	105.5	86.9 <sup>a</sup>
3e 6-NO <sub>2</sub>	1	135.0	111.2 <sup>b</sup>
	10	145.0	119.4 <sup>a</sup>
	100	121.5	100.1
3h *6-CH <sub>3</sub>	1	126.0	103.8
	10	101.0	83.2 <sup>a</sup>
	100	22.0	18.1 <sup>a</sup>
abscisic acid (ABA) standard	1	95.4	78.6 <sup>a</sup>
	10	77.4	63.7 <sup>a</sup>
	100	45.2	57.2 <sup>a</sup>

\*Benzoxazole derivative

Values followed by the letter a or b are significantly different at the 1 % or 0.5 % level against the control as determined by Student's t-test.

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