Preparation, Infrared Spectra, and Growth-Regulating Activity of 2-Substituted Benzimidazoles

^{a}M. LÁCOVÁ, ^{a}S. ABLIAMI, ^{a}A. PERJÉSSY, ^{b}K. KRÁĽOVÁ, and ^{a}J. CHOVANCOVÁ

^{a}Department of Organic Chemistry, Faculty of Natural Sciences, Comenius University, SK-842 15 Bratislava

^{b}Institute of Chemistry, Faculty of Natural Sciences, Comenius University, SK-842 15 Bratislava

A modified method was proposed to prepare 2-arylbenzimidazoles, 2-(aryl-Y-methyl)benzimidazoles, and some of their 1-ethoxycarbonyl derivatives. The condensation reactions of 2-methylbenzimidazole, 2-(aryloxymethyl)benzimidazole, and 2-(arylthiomethyl)benzimidazole with aromatic aldehydes and phthalic anhydride were also investigated. For series of prepared 2-arylbenzimidazoles the N—H stretching frequencies were correlated with substituent constants of the aryl moiety. The synthesized compounds exhibit moderate growth-stimulating activity on the roots and cotyledons of Zea mays L.

Most of benzimidazoles owing to their biological activity are significant compounds. Though benzothiazole and its derivatives resemble the structure of purines, their biological activity can be antagonistic to that of purine bases. For instance, it was observed that the growth of fungi caused by benzimidazole disappeared by addition of adenine or guanine [1]. It is known that some benzimidazoles exhibit several antimicrobial, antiparasitical, antifungal, antiulcer, analgetical, cardiovascular, and antiasthmatic activities like drugs used in human as well as in veterinary medicine [2, 3].

Benzimidazoles are also remarkable because of their low toxicity. E.g. the wide-spectral antifungal and antiparasitical 2-thiazolylbenzimidazole, which is employed under a commercial name Thiabendazol, shows [4] an LD_{50} for rats 3330 mg kg^{-1}, for mice 3810 mg kg^{-1}, and for rabbits 3850 mg kg^{-1}. Due to a low toxicity for mammals benzimidazole derivatives began to be widely used as plant-protecting media, e.g. herbicides and fungicides [4], insecticides and acaricides [5, 6].

The infrared spectra of 5- and 6-substituted benzimidazoles were investigated [7]. The absorption bands of N—H stretching vibration measured in solid state were observed in the region of $\tilde{v}$ = 2400—3200 cm^{-1}, which indicates that the compounds are bonded by intermolecular hydrogen bonds of the —N—H···N= type. The spectra of compounds in solutions of CH_2Cl_2 and $Cl_2C=CCl_2$ exhibit absorption bands of v(N—H) vibration of the free N—H groups in the region of $\tilde{v}$ = 3420—3470 cm^{-1}. The electron-donating substituents increase and the electron-withdrawing ones decrease the position of the above bands. The electron density in position 2 of benzimidazole skeleton is most markedly influenced by substituents, while that in position 4 is only less influenced and in the position 5 practically no changes can be observed.
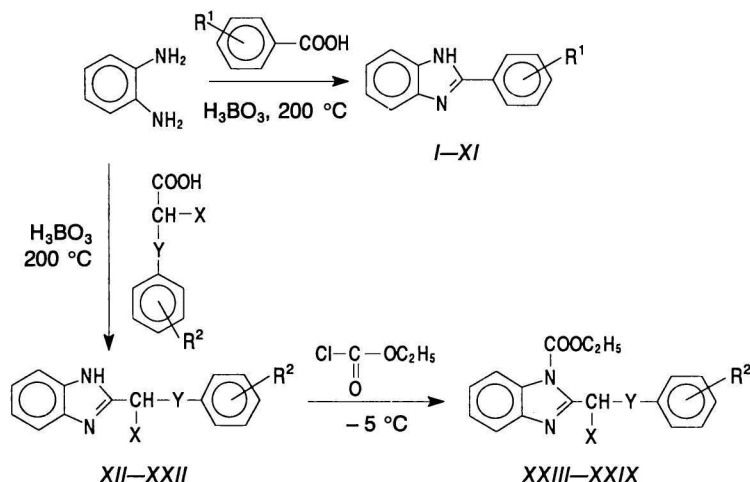
With regard to the high biological activity and low toxicity it seems to be uninterruptedly topical to investigate the relations between the structure and the spectral and biological properties in series of substituted benzimidazoles. The present work was therefore aimed to prepare 2-arylbenzimidazoles (I—XI) and investigate the transmission of electronic effects in the benzimidazole system using infrared spectra in the region of N—H stretching vibrations (Scheme 1). The further goal of the work was to synthesize in analogical way 2-(aryloxymethyl)- and 2-(arylthiomethyl)benzimidazoles (XII—XXII) and their 1-ethoxycarbonyl derivatives (XXIII—XXIX) and compare the influence of oxygen and sulfur bridges on the yields of products as well as to investigate the growth-regulating activity for all synthesized substances.

EXPERIMENTAL

The infrared spectra of compounds I—VIII were taken in the region of $\tilde{v}$ = 3100—3500 cm^{-1} on a Zeiss M 80 spectrometer at room temperature. For measurements solutions in trichloromethane (purified and dried in usual manner) and NaCl cells of 1 cm and 2 cm thickness were used. The concentration of measured solutions was chosen to reach transmittance between 25 % and 30 % for investigated bands. Peak positions were determined with an accuracy of ± 0.1 cm^{-1}. The data together with substituent constants are listed in Table 2.

^{1}H NMR spectra were measured on Tesla BS 487 A (80 MHz) instrument. The results are summarized in Table 3.

	R¹			R²	X	Y
I	4-N(C₂H₅)₂		XII	2,4,5-Cl₃	H	O
II	4-OCH₃		XIII	2-CH₃-4-Cl	H	O
III	4-CH₃		XIV	2,4-Cl₂	CH₃	O
IV	H		XV	2-CH₃-4-Cl	CH₃	O
V	3-Cl		XVI	3-NO₂	H	O
VII	3-NO₂		XVII	2,4-(NO₂)₂	H	O
VIII	4-NO₂		XVIII	2-CH(CH₃)₂-5-CH₃	H	O
IX	4-Cl		XIX	4-Cl	CH₃	O
X	3-OCH₃		XXI	H	H	S
			XXII	4-Cl	H	S
			XXIII	2,4,5-Cl₃	H	O
VI — 2-(3-pyridyl)benzimidazole			XXIV	2-CH(CH₃)₂-5-CH₃	H	O
XI — 2-(1-naphthyl)benzimidazole			XXV	2-CH₃-4-Cl	H	O
XX — 2-((2-naphthyloxy)-1-ethyl)benzimidazole			XXVII	3-NO₂	H	O
XXVI — 1-ethoxycarbonyl-2-((2-naphthyloxy)-1-ethyl)benzimidazole			XXVIII	H	H	S
			XXIX	4-Cl	H	S

Scheme 1

In the biological tests the seeds of maize (*Zea mays* L.) were moistened for 12 h in solutions of appertaining compounds. Afterwards they were soon on filter paper, coiled up, placed into the perforated polyethylene bags and hanged for 4 d. After expiration of the above time the length of roots and the above-ground parts of plants were measured. The results of measurements were evaluated in percentage against to the reference sample. Because of the low solubility of compounds in water the tested solutions were prepared by dilution of solutions of compounds in dimethylformamide of $c = 10^{-2}$ mol dm^{-3} by water. The reference sample was cultivated in dilute dimethylformamide. The results are listed in Table 4.

2-Arylbenzimidazoles (*I—XI*) and 2-(Aryl-Y-methyl)benzimidazoles (*XII—XXII*)

A reaction mixture consisting of 1,2-diaminobenzene (10 mmol), corresponding carboxylic acid (10 mmol), and boric acid (2 mmol) was heated for 5 h at 200—210 °C under stirring and removal of water formed during the reaction. After completion of the reaction the mixture was cooled down by addition

of water (50 cm³), refluxed for 30 min and cooled down again to 50 °C. The precipitate was sucked off and recrystallized from the mixture of ethanol and water. The yield was 80—90 %. The physical and analytical properties of prepared novel compounds are given in Table 1 and those of the known ones are in agreement with the data published earlier [8, 9].

1-Ethoxycarbonyl-2-(aryl-Y-methyl)benzimidazoles (*XXIII—XXIX*)

A mixture of 2-(aryl-Y-methyl)benzimidazoles (2 mmol) (or compounds *XXXVI* and *XLII*), ethyl chloroformate (2 mmol), and triethylamine (2 mmol), acetone (15 cm³), and dimethylformamide (1 cm³) was stirred for 1 h at − 5 °C. The precipitate was recrystallized from acetone or a mixture of cyclohexane—ethanol. The physical and analytical properties of synthesized compounds are given in Table 1.

2-(2-Hydroxy-2-(R³-phenyl)ethyl)benzimidazoles (*XXX—XXXIV*)

A mixture of 2-methylbenzimidazole (1.4 g; 10 mmol), corresponding R³-phenylcarbaldehyde (11

Table 1. Newly Prepared Benzimidazole Derivatives

Compound	Formula M_r	w_i(calc.)/% w_i(found)/%				M.p./°C
		C	H	N	Cl	
XII	$C_{14}H_9Cl_3N_2O$ 327.59	51.32 51.10	2.76 2.48	8.55 8.53	32.46 32.44	191—193
XIII	$C_{15}H_{13}ClN_2O$ 272.70	66.05 66.28	4.80 4.64	10.27 10.35	12.90 12.68	227—228
XIV	$C_{15}H_{12}Cl_2N_2O$ 307.18	58.65 58.89	3.94 4.00	9.18 9.06	23.08 22.94	202—204
XV	$C_{16}H_{15}ClN_2O$ 286.76	67.01 67.15	5.27 5.24	9.76 9.71	12.36 12.50	226—228
XVI	$C_{14}H_{11}N_3O_3$ 229.26	62.45 63.30	4.12 4.10	15.60 15.81	– –	173—175
XVII	$C_{14}H_{10}N_4O_5$ 284.20	54.89 54.64	2.81 2.78	19.70 19.56	– –	315—317
XVIII	$C_{18}H_{20}N_2O$ 250.22	81.60 81.47	7.20 7.15	11.20 11.36	– –	148—149
XIX	$C_{15}H_{13}ClN_2O$ 272.70	66.05 66.20	4.80 4.64	10.27 10.35	12.90 12.68	209—210
XX	$C_{19}H_{16}N_2O$ 288.22	79.10 79.34	5.55 5.42	9.71 9.56	– –	227—228
XXI	$C_{14}H_{12}N_2S$ 240.26	69.94 70.15	4.99 5.12	11.65 11.84	– –	136—137
XXII	$C_{14}H_{11}ClN_2S$ 274.71	61.15 61.34	4.00 4.18	10.19 10.29	12.88 12.99	184—186
XXIII	$C_{17}H_{13}Cl_3N_2O_3$ 399.66	51.09 50.94	3.27 3.17	7.00 6.88	26.61 26.57	146—148
XXIV	$C_{21}H_{24}N_2O_3$ 352.20	71.55 71.41	6.81 6.63	7.95 7.81	– –	98—99
XXV	$C_{18}H_{17}ClN_2O_3$ 344.80	62.70 62.77	4.96 4.84	8.10 8.89	10.28 10.27	92—95
XXVI	$C_{22}H_{20}N_2O_3$ 360.41	73.32 73.56	5.59 5.68	7.77 7.94	– –	98—101
XXVII	$C_{17}H_{15}N_3O_5$ 341.32	59.82 59.61	4.43 4.54	12.31 12.48	– –	144—145
XXVIII	$C_{17}H_{16}N_2O_2S$ 312.39	65.36 65.22	5.16 5.28	8.97 8.92	– –	69—70
XXIX	$C_{17}H_{15}ClN_2O_2S$ 346.84	58.87 58.65	4.36 4.48	8.08 8.25	10.22 10.46	80—81
XXX	$C_{16}H_{16}N_2O$ 252.20	76.16 76.19	6.39 6.14	11.10 11.15	– –	196—198
XXXI	$C_{16}H_{16}N_2O_2$ 268.20	71.59 71.33	5.96 5.59	10.44 10.41	– –	190—192
XXXII	$C_{15}H_{13}ClN_2O$ 272.70	66.07 66.31	4.77 4.74	10.27 10.13	12.99 12.87	215—218
XXXIII	$C_{15}H_{13}ClN_2O$ 272.70	66.07 66.22	4.77 4.80	10.27 10.27	12.99 12.75	232—233
XXXIV	$C_{15}H_{13}N_3O_3$ 283.30	63.60 63.72	4.62 4.57	14.83 14.82	– –	211—213
XXXV	$C_{15}H_{12}N_2$ 220.20	81.79 81.55	5.49 5.48	12.71 12.78	– –	199—202
XXXVI	$C_{16}H_{14}N_2$ 234.20	81.98 81.63	5.97 5.78	11.95 11.88	– –	221—223
XXXVII	$C_{15}H_{11}ClN_2$ 254.70	70.73 70.48	4.35 4.44	10.99 10.63	13.92 13.33	223—225
XXXVIII	$C_{15}H_{11}ClN_2$ 254.70	70.73 70.51	4.35 4.43	10.99 10.69	13.92 13.45	226—228
XXXIX	$C_{16}H_{14}N_2O$ 250.30	76.78 76.54	5.64 5.63	11.19 10.89	– –	205—207
XL	$C_{17}H_{17}N_3$ 204.20	77.56 77.28	6.46 6.50	15.96 15.67	– –	139—141
XLI	$C_{19}H_{21}N_3$ 291.30	78.31 78.08	7.26 7.30	14.42 14.68	– –	240—242

Table 1   (Continued)

Compound	Formula M_r	w_i(calc.)/% w_i(found)/%				M.p./°C
		C	H	N	Cl	
XLII	$C_{15}H_{11}N_3O_2$ 265.20	67.87 67.52	4.14 4.08	15.84 15.72	– –	325—327
XLIII	$C_{15}H_{11}N_3O_2$ 265.20	67.87 67.64	4.14 4.22	15.84 15.65	– –	199—202
XLIV	$C_{18}H_{15}N_3O_4$ 337.30	64.03 63.75	4.44 4.38	12.45 12.32	– –	182—183
XLV	$C_{19}H_{18}N_2O_2$ 306.20	74.52 74.38	5.94 5.71	9.14 9.02	– –	136—137
XLVI	$C_{16}H_{10}N_2O_2$ 262.20	73.22 73.10	3.81 3.62	10.67 10.43	– –	360 (decomp.)
XLVII	$C_{22}H_{13}ClN_2O_2$ 372.70	67.96 67.80	3.37 3.65	7.22 7.52	9.51 9.21	299—302
XLVIII	$C_{22}H_{13}N_3O_5$ 399.30	66.16 65.92	3.26 3.14	10.52 10.31	– –	264—266

For compound XXVIII w_S(calc.)/%: 10.26; w_S(found)/%: 10.39; for XXIX w_S(calc.)/%: 9.24; w_S(found)/%: 9.02.

mmol), and H_3BO_3 (1 mmol) was heated and stirred at 160 °C for 2.5 h. After cooling of the reaction mixture the product was crystallized from ethanol. The yield was 60—70 %. (Higher yields were obtained (75—80 %) by adding of nitrobenzene (5—10 cm^3) to the reaction mixture. After the reaction nitrobenzene must be separated by distillation.)

2-(R^3-Styryl)benzimidazoles (XXXV—XLIII)

A mixture of 2-methylbenzimidazole (1.4 g; 10 mmol), corresponding R^3-phenylcarbaldehyde (11 mmol), and boric acid (1 mmol) was heated and stirred at 210—220 °C for 4 h. After cooling of the reaction mixture the product was crystallized from dioxane. The yield was ca. 70—75 %.

Reaction of Phthalic Anhydride with 2-(Aryl-Y-methyl)benzimidazoles

The mixture of the freshly melted phthalic anhydride (3 g; 20 mmol), 2-(aryl-Y-methyl)benzimidazole (10 mmol), and boric acid (1 mmol) or CH_3COOK (1 mmol) was heated at 180—190 °C for 3 h. After cooling of the reaction mixture the solid product was washed with warm water, then crystallized from the ethanol—dimethyl sulfoxide mixture. Products XLVI—XLVIII are in Table 1.

RESULTS AND DISCUSSION

The compounds I—XXII (see Tables 1—3) were prepared by modification of procedures published previously [6, 8—10]. The modification consisted of the prolongation of reaction time from 4 h to 6 h and use of boric acid instead of more acidic $POCl_3$ or

polyphosphoric acid [6, 10]. The above procedure appeared convenient because the yields comparable with those published in literature (i.e. 45—65 %) were obtained. The modified method is particularly advantageous for synthesis of 2-(aryloxymethyl)-benzimidazoles (XII—XX) (Table 1) arising in the yields of 80—88 %. The 2-(arylthiomethyl) derivatives (XXI, XXII) originated in the yields of 70—72 %. The only exceptions were 2-(4-nitrophenoxymethyl)- (XVI) and 2-(2,4-dinitrophenoxymethyl)benzimidazole (XVII) obtained in the yields of 40 % and 15 %, respectively. The carbethoxylation of some of the compounds XII—XXII afforded 1-ethoxycarbonyl derivatives (XXIII—XXIX) in the yields of 90—95 % under experimental conditions described in Experimental. By this reaction it is important to use triethylamine diluted in acetone and add it dropwise to the reaction mixture under cooling. The purpose of carbethoxylation on the nitrogen atom of benzimidazole ring was to increase the lipophilicity of compounds and possibly rise their growth-regulating activity.

The condensation reactions of 2-methyl-, 2-(aryl-oxymethyl)-, or 2-(arylthiomethyl)benzimidazole with aromatic aldehydes or phthalic anhydride were studied. We found that acetic anhydride cannot be used as the reaction medium, therefore the imidazole ring is acylating and opening. By reaction of the aromatic aldehydes with 2-methylbenzimidazole the aldol or condensation products or a mixture of both of them were isolated. The conditions of these reactions are described in Experimental.

The main aldol products were obtained at reaction temperature of 160 °C or at the temperature of refluxing nitrobenzene. The major condensation products occurred at 200—220 °C. The aldol products are not stable in acidic media. The heating of aldol products (60—80 °C) in acetic acid led to anhydro derivatives, which can be regarded as a suitable

Table 2. The N—H Stretching Frequencies (in CHCl₃) and Corresponding Substituent Constants for 2-Arylbenzimidazoles (*I—VIII*)

Compound	$\tilde{v}(v(N—H))/cm^{-1}$	σ^a	$\sigma^{+\,b}$	$\sigma^{-\,c}$	$\mathcal{F}^a$	$\mathcal{R}^a$
I	3474.2	− 0.90	− 1.42	− 0.90	0.01	− 0.91
II	3470.0	− 0.27	0.78	0.27	0.26	− 0.51
III	3470.0	− 0.17	− 0.31	− 0.17	− 0.04	− 0.13
IV	3459.3	0.00	0.00	0.00	0.00	0.00
V	3467.0	0.37	0.40	0.49	0.41	0.00
VI	3466.0	0.62^d	0.62^e	0.76	–	–
VII	3465.5	0.71	0.67	0.71	0.67	0.00
VIII	3465.0	0.78	0.79	1.27	0.67	0.16

a) Taken from Ref. [11]; *b*) [12]; *c*) [13]; *d*) [14]; *e*) [15].

Table 3. ¹H NMR Spectra of 2-Substituted Benzimidazoles

Compound	Solvent	δ
XII	DMSO-d_6	2.23 (s, 3H), 5.34 (s, 2H), 7.13—7.52 (m, 7H)
XIV	DMSO-d_6	1.76 (d, 3H, J = 6 Hz), 5.6—5.8 (q, 1H), 7.10—7.59 (m, 7H)
XV	DMSO-d_6	1.74 (d, 3H, J = 6 Hz), 2.24 (s, 3H), 5.55—5.80 (q, 1H), 7.10—7.49 (m, 7H)
XVI	CDCl₃	5.46 (s, 2H), 7.25—7.92 (m, 8H), 9.75 (br, 1H)
XVIII	CDCl₃	1.14 (d, 6H, J = 6 Hz), 2.23 (s, 3H), 3.29 (q, 1H, J = 7.5 Hz), 5.32 (s, 2H), 7.04—7.70 (m, 7H)
XXIII	DMSO-d_6	1.06 (t, 3H, J = 6 Hz), 3.42—3.51 (q, 2H, J = 7 Hz), 5.48 (s, 2H), 7.12—7.32 (m, 2H), 7.52—7.67 (m, 2H), 7.73 (s, 1H), 7.79 (s, 1H)
XXIV	CDCl₃	1.16 (d, 6H, J = 6 Hz), 1.37 (t, 3H, J = 6 Hz), 2.32 (s, 3H), 3.25 (quin., 1H, J = 6 Hz), 4.43 (q, 1H, J = 6 Hz), 5.50 (s, 2H), 7.06—7.9 (m, 7H)
XXV	DMSO-d_6	1.3 (t, 3H, J = 6 Hz), 2.15 (s, 3H), 4.45 (q, 2H, J = 7 Hz), 5.54 (s, 2H), 7.11—7.46 (m, 7H)
XXVI	CDCl₃	1.49 (t, 3H, J = 5 Hz), 1.50 (d, 3H, J = 5 Hz), 4.45 (q, 2H, J = 6 Hz), 6.38 (q, 1H, J = 6 Hz), 7.16—7.89 (m, 11H)
XXVII	CDCl₃	1.49 (t, 3H, J = 6 Hz), 4.58 (q, 2H, J = 6 Hz), 5.64 (s, 2H), 7.33—7.92 (m, 7H)
XXVIII	CDCl₃	1.51 (t, 3H, J = 6 Hz), 4.62 (s, 2H), 4.54 (q, 2H, J = 6 Hz), 7.16—7.86 (m, 9H)
XXIX	CDCl₃	1.53 (t, 3H, J = 8 Hz), 4.59 (s, 2H), 4.55 (q, 2H, J = 8 Hz), 7.13—7.67 (m, 8H)
XXXI	DMSO-d_6	1.71 (d, 2H, J = 6 Hz), 2.22 (s, 3H), 5.65 (q, 1H, J = 4 Hz), 7.03—7.46 (m, 8H)
XXXII	DMSO-d_6	3.14 (d, 2H, J = 6 Hz), 5.17 (q, 1H, J = 6 Hz), 5.82 (d, 1H, J = 6 Hz), 7.05—7.54 (m, 8H)
XXXIII	DMSO-d_6	3.11 (d, 2H, J = 6 Hz), 5.12 (q, 1H, J = 6 Hz), 5.74 (d, 1H, J = 4 Hz), 7.37 (s, 4H), 7.05—7.16 (m, 2H), 7.42—7.53 (m, 2H)
XXXIV	DMSO-d_6	3.15 (d, 2H, J = 6 Hz), 5.27 (q, 1H, J = 6 Hz), 5.95 (d, 1H, J = 6 Hz), 7.08—8.25 (m, 8H)
XXXV	CDCl₃	7.25—7.70 (m, 11H), 10.5 (br, 1H, NH)
XXXV	DMSO-d_6	7.07—7.65 (m, 11H)
XXXVI	CDCl₃	2.31 (s, 3H), 7.02—7.64 (m, 10H), 8.46 (br, 1H)
XXXVII	DMSO-d_6	7.13—7.75 (m, 10H)
XXXVIII	DMSO-d_6	7.12—7.72 (m, 10H), 12.6 (br, 1H, NH)
XXXIX	DMSO-d_6	3.76 (s, 3H), 6.72—7.74 (m, 10H)
XL	CDCl₃	2.98 (s, 6H), 6.50—7.87 (m, 10H)
XLI	DMSO-d_6	1.12 (t, 6H, J = 8 Hz), 3.40 (q, 4H, J = 8 Hz), 6.8—8.02 (m, 10H)
XLIII	DMSO-d_6	7.06—8.75 (m, 10H), 9.06 (br, 1H, NH)
XLIV	CDCl₃	1.58 (t, 3H, J = 6 Hz), 4.61 (q, 2H, J = 6 Hz), 7.29—8.43 (m, 10H)
XLV	CDCl₃	1.50 (t, 3H, J = 6 Hz), 2.77 (s, 3H), 4.57 (q, 2H, J = 8 Hz), 7.23—7.92 (m, 10H)
XLVI	DMSO-d_6	7.26—7.82 (m, 9H)

method for preparation of pure condensation products from reaction mixtures. We found that 2-(aryl-thiomethyl)benzimidazole with phthalic anhydride gave 2-(2-benzimidazolyl)-1,3-indandione (*XLVI*) with simultaneous removing of arylthio group. No products were obtained from the reaction of 2-(aryloxymethyl)benzimidazole with aromatic aldehydes. However, using phthalic anhydride 3-((2-benzimidazole)aryl-oxymethylene) phthalides (*XLVII, XLVIII*) were obtained (Scheme 2).

The results of biological tests (Table 4) show that 2-(2,4,5-trichlorophenoxymethyl)benzimidazole (*XII*) possesses the highest activity; the growth of the roots

being by 35 % higher compared to the reference sample. It can be generally stated that the concentration of the tested compound c = 10⁻⁴ mol dm⁻³ moderately stimulates the growth of the roots and cotyledons of *Zea mays*. A distinct stimulating activity appears almost at all tested compounds at the concentration c = 1 × 10⁻⁷ mol dm⁻³; it decreases again at the concentration c = 1 × 10⁻⁹ mol dm⁻³. Practically no change of growth-regulating activity was observed by the introduction of ethoxycarbonyl group into the structure of 2-(aryl-Y-methyl)benzimidazoles. The aldol and the condensation products are also stimulating with respect to the growth of plants (Table 4).

	R^3
XXX	4-CH$_3$
XXXI	4-OCH$_3$
XXXII	3-Cl
XXXIII	4-Cl
XXXIV	3-NO$_2$
XXXV	H
XXXVI	4-CH$_3$
XXXVII	3-Cl
XXXVIII	4-Cl
XXXIX	3-OCH$_3$
XL	4-N(CH$_3$)$_2$
XLI	4-N(C$_2$H$_5$)$_2$
XLII	4-NO$_2$
XLIII	3-NO$_2$
XLIV	3-NO$_2$
XLV	4-CH$_3$
	R^2
XLVII	3-NO$_2$
XLVIII	4-Cl

Scheme 2
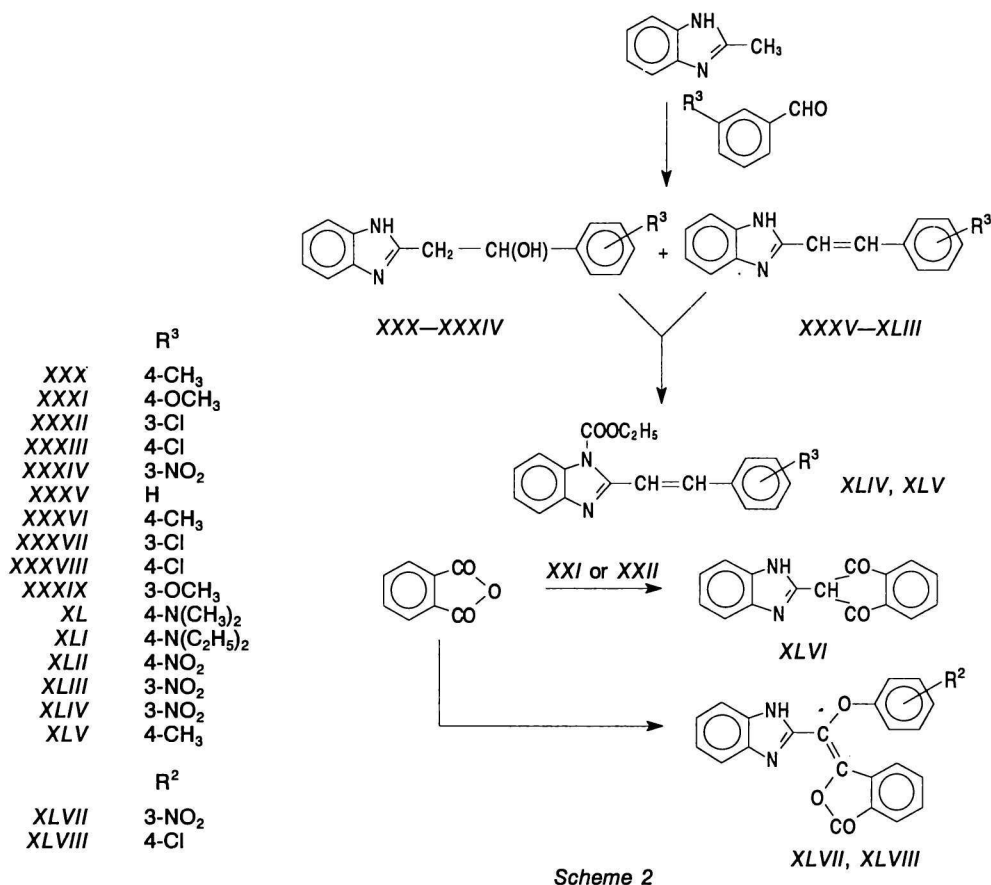
The relatively high values of N—H stretching frequencies of compounds *I—VIII* (Table 2) indicate that the benzimidazole N—H group exists in the form free of intermolecular hydrogen bonds. The electron-withdrawing substituents (aryl groups) decrease and the electron-donating ones increase the values of N—H stretching frequencies, which is in accordance with the classical conception on the transmission of substituent effects, as well as with the results published earlier [7]. The above data were correlated with Hammett σ, electrophilic σ^+ and nucleophilic σ^- substituent constants using one-parameter correlation equations

$$\nu(N—H) = \rho\sigma + q \qquad (1)$$

Table 4. Growth-Regulating Activity (a_1 for roots, a_2 for leaves) of Prepared Compounds in % of Reference Sample

Compound	a_1/% c/(mol dm^{-3})			a_2/% c/(mol dm^{-3})		
	10^{-4}	10^{-7}	10^{-9}	10^{-4}	10^{-7}	10^{-9}
XII	109	135	98	109	128	99
XIII	110	115	103	105	116	110
XIV	81	126	101	119	122	102
XV	72	115	110	80	108	104
XVI	96	108	101	89	115	108
XX	78	108	110	94	108	101
XXII	64	119	108	116	122	99
XXIII	86	116	98	111	121	104
XXV	64	121	105	102	116	103
XXVI	98	106	103	101	122	106
XXVII	94	112	104	110	115	103
XXVIII	88	112	108	101	100	100
XXIX	78	92	106	102	100	100
XXXII	108	120	103	110	116	103
XXXV	106	116	101	102	108	103
XL	111	115	103	100	112	98
XLI	100	105	80	96	104	103
XLV	99	113	98	110	116	101

Table 5. Results of Statistical Treatment of Linear Correlations for Series of 2-Arylbenzimidazoles

Correlation equation	n [a]	r [b]	s/cm^{-1} [c]	ρ/cm^{-1} [d]	q/cm^{-1} [e]
(1)	8	0.996	0.29	− 5.29 ± 0.19	3469.1
(2)	8	0.975	0.74	− 3.84 ± 0.36	3468.4
(3)	8	0.976	0.72	− 4.34 ± 0.39	3469.4
(4)	7	0.997	0.31	− 5.48 ± 0.48 [f]	3469.2
				− 5.19 ± 0.40 [g]	

a) Number of experimental points used in correlations; b) correlation coefficient; c) standard deviation; d) slope; e) intercept; f) $\rho = \rho_{\mathscr{F}}$; g) $\rho = \rho_{\mathscr{R}}$.

$$\nu(N—H) = \rho\sigma^+ + q \qquad (2)$$
$$\nu(N—H) = \rho\sigma^- + q \qquad (3)$$

The results of statistical treatment of the above correlations are listed in Table 5 and the dependence of statistically most significant relations is graphically illustrated in Fig. 1. It follows from the above results that the most significant correlation was obtained ($r = 0.996$) when original Hammett σ constants are used. This indicates that the electronic effects of aryl group are transmitted to N—H group of the benzimidazole ring approximately equally well by both the inductive and resonance mechanism.

Fig. 1. Plot of N—H stretching frequencies against Hammett σ substituent constants for 2-arylbenzimidazoles (I—VIII).
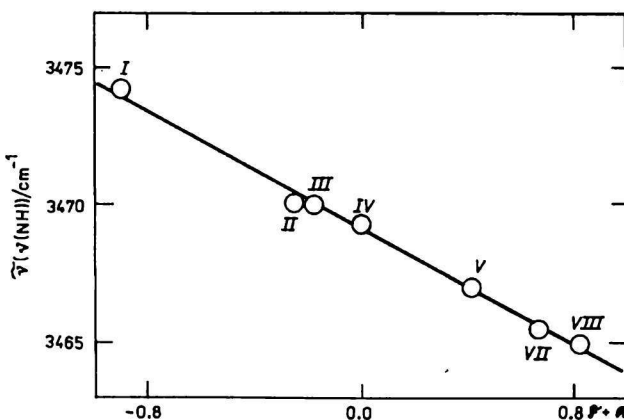
Fig. 2. Swain—Lupton correlation of N—H stretching frequencies of 2-arylbenzimidazoles (I—V, VII, and VIII).

To separate the field and resonance effects the N—H stretching frequencies of 2-arylbenzimidazoles were correlated with $\mathscr{F}$ and $\mathscr{R}$ substituent constants of the Swain—Lupton equation

$$\nu(N—H) = \rho\mathscr{F} + \rho\mathscr{R} + q \qquad (4)$$

The results of correlations are given in Table 5 and illustrated in Fig. 2. For determination of the contribution of resonance effects to the transmission of total substituent effects eqn (5) was employed.

$$\% = \frac{100\Psi(\rho_{\mathscr{R}})}{\varphi|\rho_{\mathscr{F}}| + \varphi|\rho_{\mathscr{R}}|} \qquad (5)$$

where φ and ψ are defined by relations (6) and (7).

$$\varphi = \Sigma\,|\mathscr{F}| - \overline{\mathscr{F}}\,/n \qquad (6)$$
$$\psi = \Sigma\,|\mathscr{R} - \overline{\mathscr{R}}|\,/n \qquad (7)$$

where n is the number of points used in correlations and $\overline{\mathscr{F}}$ and $\overline{\mathscr{R}}$ are the arithmetic means of field and resonance constants applied in the correlation. It follows from the results that in series of 2-arylimidazoles the contribution of resonance effect is $\% \,\mathscr{R} = 45.5$, which documents that differently to 2-aryl-5H-dibenzo[d,f]-[1,3]-diazepines [16, 17] the electronic effects are transmitted approximately equally well by both the inductive (field) and resonance mechanism. From the above said it can be concluded that in 2-arylbenzimidazoles the aryl moiety is well conjugated and coplanar with benzimidazole skeleton.

REFERENCES

1. Wooley, W. J., *Biol. Chem. 152*, 225 (1944).
2. Vodrážka, J., Mozgov, I. J., and Šimúnek, J., *Veterinárna farmakológia.* (Veterinary Pharmacology.) P. 132—136. Príroda (Nature), Bratislava, 1980.
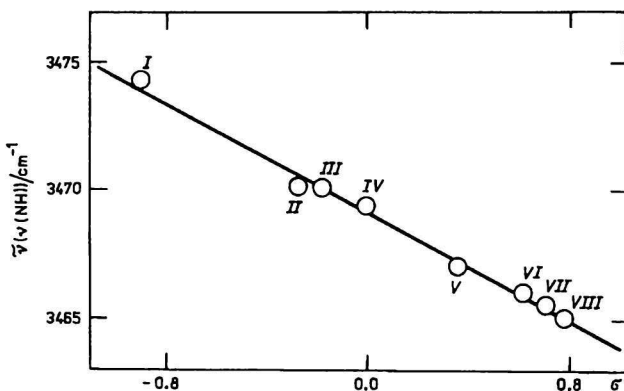3. Melichar, B., *Chemické léčivá.* (Chemical Drugs.) P. 325, 425, 667, 786. Avicenum, Prague, 1987.

4. Hubert, M., *Pesticide Manual*, 5th Edition, p. 33. British Crop Protection Council, Nothingham, 1977.
5. Hiroshi, K. and Tosihiko, Y., *Japan* 070235108 (1986); *Chem. Abstr. 104*, 186419 (1986).
6. Nikon, N., *Japan* 59172477 (1984); *Chem. Abstr. 102*, 132298 (1985).
7. Morgan, K. J., *J. Chem. Soc. 1961*, 2343.
8. Ebana, T., Jokota, K., and Takada, J., *Hokkaido Diagaku Kogakubu Kenkyu Hokoku 89*, 131 (1978); *Chem. Abstr. 91*, 157659 (1979).
9. Puskhina, L. N., Mazalov, S. A., and Postovskii, I. Yu., *Zh. Obshch. Khim. 32*, 2624 (1962).
10. Sukla, J. S., Saksena, S., and Raston, R., *Curr. Sci. 5*, 820 (1982).
11. Hansch, C. and Leo, A. J., *Substituent Constants for Correlation Analysis in Chemistry and Biology.* Wiley, New York, 1979.
12. Perjéssy, A., *Tetrahedron 29*, 3189 (1973).
13. Halgaš, J. and Perjéssy, A., *Collect. Czech. Chem. Commun. 42*, 1551 (1977).
14. Campbell, A. D., Chooi, S. Y., Deady, L. W., and Shonks, R. A., *Aust. J. Chem. 23*, 203 (1970).
15. Jaffe, H. H., *Chem. Rev. 53*, 1921 (1953).
16. O'Sullivan, D. C., *J. Chem. Soc. 1960*, 3653.
17. Popova, L. L., Sadekov, I. D., and Minkin, V. I., *Reakts. Sposobnost Organ. Soedin.* (Tartu) *5*, 682 (1968).

Translated by A. Perjéssy

Water-Soluble Polysaccharides of Poplar (*Populus alba* L.) Callus Tissue Cell Wall

Š. KARÁCSONYI

Institute of Chemistry, Slovak Academy of Sciences, SK-842 38 Bratislava

Two water-soluble arabinose-rich polysaccharides have been isolated from the primary wall of poplar (*Populus alba* L.) callus culture cells. Their structures have been investigated using chemical methods and NMR spectroscopy. The general, structural features of the polysaccharides are discussed.

Primary cell walls of plants contain considerable amounts of arabinose-rich polysaccharides as hemicellulosic components or constituents of pectic polymers [1, 2]. The occurrence of these polymers in the cell walls of actively growing cells may assume a certain nonspecified physiological function [3, 4]. In the framework of the research of cell wall polysaccharides of poplar (*Populus alba* L.) callus tissue a water-soluble, arabinose-rich fraction of pectic polymers was isolated [5]. Fractionation and structural characterization of this material is the subject of this report.

EXPERIMENTAL

Material and Methods

Cell walls were isolated from poplar (*Populus alba* L. var. *pyramidalis*) callus culture cells as described [5].

All evaporations were carried out below 40 °C. Spectral data were recorded with a Perkin—Elmer G 9836 (for IR) and a Specord UV VIS spectrometer. Optical rotations (1 cm^3 cell) were measured with a Perkin—Elmer Model 141 polarimeter at (20 ± 1) °C and $\lambda = 585$ nm, in water. Free-boundary electrophoresis of polysaccharide solutions ($\rho = 10$ mg cm^{-3}) was performed in 50 mM sodium tetraborate buffer of pH 9.2 with a Zeiss 35 apparatus for 30 min at 150 V and 8 mA. Analytical GLC separations were performed on a Hewlett—Packard Model 5711 A instrument. A stainless steel column (2.0 m × 3 mm) coated with A, 3 % of SP-2340 on Chromosorb WAW-DMCS (150—170 μm) was used with N_2 carrier-gas flow rate 30 cm^3 min^{-1}. The temperature program was 120 °C → 250 °C at 4 °C min^{-1} for the separation of fully acetylated alditols.

GLC-MS analysis was performed on a Hewlett—Packard 5985 A instrument equipped with B, OV-17 capillary glass-column (25 m × 0.21 mm) and the temperature program was 180 °C → 260 °C at 3 °C min^{-1} with initial hold of 1 min. Paper chromatography was performed on Whatman No. 1 and No. 3 MM papers, using C ethyl acetate—acetic acid—for-