SYNTHESIS OF SOME NEW CHLORO DERIVATIVES OF QUINAZOLINO[4,3-*b*]QUINAZOLIN-5-ONE AND TETRAZOLO[5,4-*c*]QUINAZOLINE

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Introducing of chlorine into biologically versatile heterocyclic rings might lead to the improvement of their pharmacological activity. Therefore compounds *IIa – IIr* and *IIIa – IIIf* were prepared with the aim to combine the pesticidal qualities of heterocyclic nuclei.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were recorded with Pye Unicam SP 1200G spectrometer in KBr pellets. The ^{1}H NMR spectra were obtained in $(CD_3)_2SO$ using Varian A-60 MHz spectrometer and tetramethylsilane as internal standard. The chemical shifts are reported in δ, ppm. The mass spectra were determined with 7070 F spectrometer using direct inlet temperature 90 °C and energy of 70 eV.

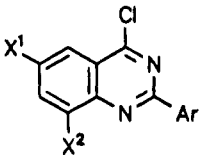
5-Chloro and 3,5-dichloroanthranilic acids were prepared according to the method adopted by Endicott et al.[1].

Reaction of 2-Aryl-4-chloroquinazolines *Ia – If* with Anthranilic Acid Derivatives: Formation of *IIa – IIr*

Equimolar amounts of 4-chloro-2-arylquinazoline derivatives (*Ia – If*) and respective anthranilic acid derivative were refluxed in glacial acetic acid for 1 h. The reaction mixture was concentrated under vacuum, cooled, and poured into ice water. The crude product thus obtained was filtered off, washed twice with water and recrystallized from ethanol–acetone mixture (60 : 40). Basic physical, analytical and spectral data of products are reported in Tables I and II.

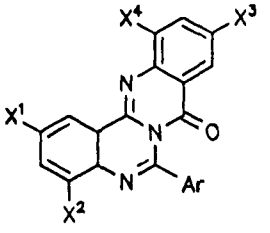
Reaction of 2-Aryl-4-chloroquinazolines *Ia – If* with Sodium Azide: Formation of *IIIa – IIIf*

An equimolar mixture of 2-aryl-4-chloroquinazoline (*Ia – If*) and sodium azide was refluxed in benzene for 5 h. The solvent was evaporated in vacuo. The oily residue was triturated several times with light petroleum. The obtained solid was washed with cold ethanol, collected, and recrystallized from ethanol. The products were identified as 5-aryltetrazolo[5,4-*c*]quinazoline derivatives (*IIIa – IIIf*). Basic physical, analytical and spectral data are reported in Tables I and II.



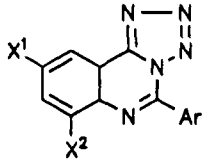
I

	X^1	X^2	Ar
a	H	H	C
b	Cl	H	C_6H_5
c	Cl	Cl	C_6H_5
d	H	H	4-Cl-C_6H_4
e	Cl	H	4-Cl-C_6H_4
f	Cl	Cl	4-Cl-C_6H_4



II

	X^1	X^2	X^3	X^4	Ar
a	H	H	H	H	C_6H_5
b	Cl	H	H	H	C_6H_5
c	H	H	Cl	H	C_6H_5
d	Cl	H	Cl	H	C_6H_5
e	Cl	Cl	H	H	C_6H_5
f	H	H	Cl	Cl	C_6H_5
g	Cl	Cl	Cl	H	C_6H_5
h	Cl	H	Cl	Cl	C_6H_5
i	Cl	Cl	Cl	Cl	C_6H_5
j	H	H	H	H	4-Cl-C_6H_4
k	Cl	H	H	H	4-Cl-C_6H_4
l	H	H	Cl	H	4-Cl-C_6H_4
m	Cl	H	Cl	H	4-Cl-C_6H_4
n	Cl	Cl	H	H	4-Cl-C_6H_4
o	H	H	Cl	Cl	4-Cl-C_6H_4
p	Cl	Cl	Cl	H	4-Cl-C_6H_4
q	Cl	H	Cl	Cl	4-Cl-C_6H_4
r	Cl	Cl	Cl	Cl	4-Cl-C_6H_4



III

	X^1	X^2	Ar
a	H	H	C_6H_5
b	Cl	H	C_6H_5
c	Cl	Cl	C_6H_5
d	H	H	4-Cl-C_6H_4
e	Cl	H	4-Cl-C_6H_4
f	Cl	Cl	4-Cl-C_6H_4

TABLE I
IR, ^{1}H NMR and mass spectral data of compounds *II* and *III*

Compound	IR spectra ν, cm^{-1}	^{1}H NMRspectra[a] δ, ppm	Mass spectra, *m/z* (%)
IIa	1 687 (C=O); 1 626 (C=N)	7.30 – 8.75	$M^{+\cdot}$ = 322 (33.4), 205 (8.2), 179 (67.8), 144 (73.1), 103 (21.2), 76 (32.13), 77 (100)
IIb	1 688 (C=O); 1 625 (C=N)	7.30 – 8.85	$M^{+\cdot}$ = 357 (62.3), 239 (8.2), 213 (42.5), 144 (65.2), 110 (82.2), 103 (100), 77 (88.3) 76 (75.6)
IIc	1 682 (C=O); 1 623 (C=N)	7.40 – 8.88	$M^{+\cdot}$ = 357 (32.8), 205 (8.9), 179 (72.3), 118 (47.2), 110 (81.4), 103 (100), 77 (92.7), 76 (32.6)
IId	1 682 (C=O); 1 625 (C=N)	7.35 – 8.70	$M^{+\cdot}$ = 391 (42.8), 239 (6.3), 213 (62.3), 184 (21.7), 110 (18.5), 103 (83.2), 77 (100)
IIe	1 683 (C=O); 1 624 (C=N)	7.30 – 8.82	$M^{+\cdot}$ = 391 (38.2), 273 (11.8) 247 (34.6), 144 (100), 103 (71.3), 77 (82.6), 76 (18.8)
IIf	1 688 (C=O); 1 624 (C=N)	7.38 – 8.84	$M^{+\cdot}$ = 391 (41.3), 212 (72.6), 205 (62.1), 179 (32.6), 144 (88.7), 103 (92.2), 77 (100), 76 (28.3)
IIg	1 686 (C=O); 1 625 (C=N)	7.40 – 8.80	$M^{+\cdot}$ = 425 (18.3), 273 (29.6), 247 (38.3), 178 (32.2), 144 (65.5), 110 (80.2), 103 (100), 77 (93.3)
IIh	1 685 (C=O); 1 627 (C=N)	7.40 – 8.81	$M^{+\cdot}$ = 425 (13.8), 239 (25.6), 213 (28.9), 212 (32.6), 144 (67.2), 110 (100), 103 (82.3), 77 (92.7)
IIi	1 685 (C=O); 1 626 (C=N)	7.38 – 8.78	$M^{+\cdot}$ = 459 (28.8), 273 (33.2) 247 (19.6), 212 (21.2), 144 (53.2), 103 (58.3), 77 (100)
IIj	1 684 (C=O); 1 625 (C=N)	7.28 – 8.80	$M^{+\cdot}$ = 356 (36.2), 238 (18.6), 212 (36.7), 144 (43.2), 137 (100), 76 (32.1)
IIk	1 685 (C=O); 1 623 (C=N)	7.33 – 8.76	$M^{+\cdot}$ = 391 (12.3), 273 (38.1), 247 (25.3), 144 (51.3), 137 (62.8), 111 (69.6), 110 (100), 76 (76.3)
III	1 980 (C=O); 1 625 (C=N)	7.38 – 8.75	$M^{+\cdot}$ = 391 (28.8), 239 (33.3), 213 (18.2), 178 (20.8), 137 (100), 111 (40.3), 110 (61.4), 76 (77.8)
IIm	1 687 (C=O); 1 630 (C=N)	7.36 – 8.68	$M^{+\cdot}$ = 425 (62.2), 383 (40.7), 257 (21.9), 178 (33.7), 111 (100), 110 (39.2)
IIn	1 684 (C=O); 1 626 (C=N)	7.42 – 8.72	$M^{+\cdot}$ = 425 (38.4), 309 (42.6), 281 (55.4), 144 (26.8), 137 (100), 76 (78.3)
IIo	1 683 (C=O); 1 626 (C=N)	7.38 – 8.78	$M^{+\cdot}$ = 425 (23.5), 239 (36.3), 213 (48.2) 212 (39.9), 144 (62.6), 137 (100), 111 (24.2), 76 (72.6).
IIp	1 680 (C=O); 1 620 (C=N)	7.30 – 8.75	$M^{+\cdot}$ = 459 (34.7), 273 (27.3), 247 (28.4), 212 (46.8), 144 (62.6), 137 (88.6), 111 (100), 110 (37.3)

TABLE I
(Continued)

Compound	IR spectra ν, cm^{-1}	^1H NMRspectra[a] δ, ppm	Mass spectra, *m/z* (%)
IIq	1 683 (C=O); 1 625 (C=N)	7.41 – 8.76	$M^{\cdot+}$ = 459 (23.6), 307 (32.8), 281 (18.6), 178 (43.5), 144 (52.6), 137 (100), 111 (81.2), 110 (63.4)
IIr	1 685 (C=O); 1 628 (C=N)	7.36 – 8.72	$M^{\cdot+}$ = 493 (32.1), 207 (24.6), 281 (19.7), 212 (72.8), 144 (56.2), 137 (100), 111 (36.3)
IIIa	1 573; 1 410 (N=N)	7.27 – 8.88	$M^{\cdot+}$ = 247 (24.8), 210 (27.4), 144 (32.2), 116 (42.8), 103 (100), 77 (93.8)
IIIb	1 575; 1 415 (N=N)	7.25 – 8.40	$M^{\cdot+}$ = 281 (38.2), 253 (45.5), 178 (65.4), 150 (65.2), 103 (88.3), 77 (100)
IIIc	1 578; 1 410 (N=N)	7.25 – 8.89	$M^{\cdot+}$ = 315 (30.6), 287 (22.8), 238 (38.6), 210 (25.1), 144 (62.3), 103 (100), 77 (89.2)
IIId	1 580; 1 415 (N=N)	7.28 – 8.92	$M^{\cdot+}$ = 281 (18.8), 253 (29.1), 170 (62.2), 142 (46.3), 137 (75.3), 111 (100), 76 (82.3)
IIIe	1 575; 1 410 (N=N)	7.35 – 8.90	$M^{\cdot+}$ = 315 (20.8), 287 (38.5), 204 (40.6), 176 (32.3), 137 (100), 111 (28.2), 100 (23.4)
IIIf	1 577; 1 410 (N=N)	7.30 – 8.44	$M^{\cdot+}$ = 344 (29.2), 321 (62.3), 238 (45.5), 240 (17.2), 210 (38.2), 144 (30.3), 137 (100), 111 (77.8)

[a] Range of aromatic protons, multiplets.

TABLE II
Physical and analytical data of compounds *II* and *III*

Compound	M. p., °C (Yield, %)	Formula (M. w.)	Calculated/Found			
			% C	% H	% N	% Cl
IIa	138 – 139 (85)	$C_{21}H_{13}N_3O$ (323.3)	78.00 78.12	4.05 4.00	13.00 13.20	– –
IIb	143 – 144 (82)	$C_{21}H_{12}ClN_3O$ (357.8)	70.49 70.53	3.38 3.13	11.74 11.60	9.91 9.98
IIc	145 – 146 (75)	$C_{21}H_{12}ClN_3O$ (357.8)	70.49 70.62	3.38 3.16	11.74 11.58	9.91 9.72

TABLE II
(Continued)

Compound	M. p., °C (Yield, %)	Formula (M. w.)	Calculated/Found			
			% C	% H	% N	% Cl
IId	156 – 157 (90)	$C_{21}H_{11}Cl_2N_3O$ (392.2)	64.30 64.28	2.83 2.75	10.71 10.53	18.08 18.00
IIe	148 – 149 (74)	$C_{21}H_{11}Cl_2N_3O$ (392.2)	64.30 64.32	2.83 2.68	10.71 10.62	18.08 18.12
IIf	160 – 161 (69)	$C_{21}H_{11}Cl_2N_3O$ (392.2)	64.30 64.38	2.83 2.56	10.71 10.80	18.08 18.20
IIg	178 – 179 (70)	$C_{21}H_{10}Cl_3N_3O$ (426.7)	59.11 59.10	2.36 2.28	9.85 9.70	24.93 24.70
IIh	183 – 184 (78)	$C_{21}H_{10}Cl_3N_3O$ (426.6)	59.11 59.22	2.36 2.30	9.85 9.78	24.93 24.82
IIi	203 – 204 (65)	$C_{21}H_9Cl_4N_3O$ (461.1)	54.69 54.57	1.97 1.90	9.11 9.10	30.76 30.62
IIj	188 – 189 (78)	$C_{21}H_{12}ClN_3O$ (357.8)	70.49 70.32	3.38 3.20	11.74 11.80	9.91 9.74
IIk	211 – 212 (72)	$C_{21}H_{11}Cl_2N_3O$ (392.2)	64.30 64.50	2.83 2.77	10.71 10.82	18.08 18.33
IIl	216 – 217 (76)	$C_{21}H_{11}Cl_3N_3O$ (392.2)	64.30 64.24	2.83 2.68	10.71 10.60	18.08 18.40
IIm	228 – 229 (82)	$C_{21}H_{10}Cl_3N_3O$ (436.7)	57.75 57.62	2.31 2.20	11.91 11.80	24.36 24.40
IIn	240 – 241 (69)	$C_{21}H_{11}Cl_3N_3O$ (436.6)	57.75 57.90	2.31 2.34	11.91 11.73	24.36 24.48
IIo	261 – 262 (73)	$C_{21}H_{10}Cl_3N_3O$ (436.6)	57.72 57.75	2.31 2.20	11.91 11.68	24.36 24.20
IIp	268 – 269 (87)	$C_{21}H_9Cl_4N_3O$ (461.1)	54.69 54.38	1.97 1.80	9.11 9.10	30.76 30.58
IIq	282 – 283 (73)	$C_{21}H_9Cl_4N_3O$ (461.1)	54.69 54.50	1.97 1.89	9.11 9.96	30.76 30.38
IIr	294 – 295 (86)	$C_{21}H_8Cl_5N_3O$ (465.6)	50.89 50.73	1.63 1.50	8.48 8.52	35.77 35.65
IIIa	152 – 153 (69)	$C_{14}H_9N_5$ (244.3)	68.00 68.14	3.67 3.58	28.33 28.24	– –

TABLE II
(Continued)

Compound	M. p., °C (Yield, %)	Formula (M. w.)	Calculated/Found			
			% C	% H	% N	% Cl
IIIb	182 – 183 (60)	$C_{14}H_8ClN_5$ (281.7)	59.69 59.58	2.68 2.80	24.86 24.72	12.59 12.52
IIIc	198 – 199 (63)	$C_{14}H_7Cl_2N_5$ (316.2)	53.18 53.08	2.23 2.18	22.16 22.18	22.43 22.30
IIId	206 – 207 (93)	$C_{14}H_8ClN_5$ (281.7)	59.69 59.50	2.86 2.68	24.86 24.62	12.59 12.66
IIIe	218 – 219 (68)	$C_{14}H_7Cl_2N_5$ (316.2)	53.18 53.24	2.32 2.20	22.16 22.33	22.43 22.28
IIIf	242 – 243 (76)	$C_{14}H_6Cl_3N_5$ (350.6)	47.46 47.88	1.73 1.76	14.98 14.87	30.33 30.20

REFERENCES

1. Endicott M. M., Alden B. B., Sherill M. L.: J. Am. Chem. Soc. *63*, 1303 (1946).