SYNTHESIS OF NOVEL 4-AMINO-5-(DISUBSTITUTED AMINO)--2-PHENYL-2*H*-PYRIDAZIN-3-ONES

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Substituted 4-amino-2-phenyl-2*H*-pyridazin-3-ones **5a–5j** have been prepared from 4-amino-5-chloro-2-phenyl-2*H*-pyridazin-3-one **1** which on reactions with acetyl chloride or acetic anhydride gives 4-acetylamino derivative **2** or 4-diacetylamino derivative **3**, respectively. Derivatives **2** and **3** with dialkylamines and cyclic amines yielded appropriate 4-acetylamino-5-(disubstituted amino)-2-phenyl-2*H*-pyridazin-3-ones **4a–4j**. Subsequent alkaline hydrolysis of the acetylamino derivatives **4a–4j** let to the title compounds **5a–5j**, which were screened for pesticidal activity, but none of them reached activity of the used standards.

Key words: 2*H*-Pyridazin-3-ones; Diazines; Pesticidal activity.

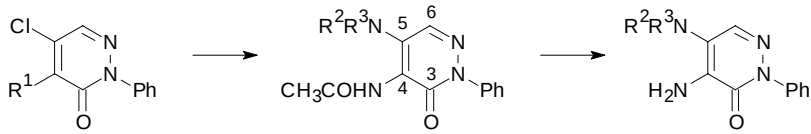
It is known that pyridazin-3-one derivatives have been in the foreground of scientific research since 1970 (refs[1–10]). One reason was a production of 5-amino-4-chloro-2-phenyl-2*H*-pyridazin-3-one (Pyramin) and its use as the herbicide by cultivating of sugar beet[11–14]. In the present communication, the starting inactive isomer 4-amino-5-chloro-2-phenyl-2*H*-pyridazin-3-one[15] **1** with acetyl chloride gave the corresponding 4-acetylamino derivative **2** and with acetic anhydride the diacetylamino compound **3** (Scheme 1).

The reaction of 4-diacetylamino-5-chloro-2-phenyl-2*H*-pyridazin-3-one **3** with secondary or cyclic amines in molar ratio 1:2 afforded compounds **4a–4j** as the main products and the compound **2** as the by-product. The reaction of compounds **4a–4j** with bases such as trialkylamine, sodium hydroxide or sodium alcoholate in alcohol, water or in their mixture from which sodium ethanolate appeared to be the most convenient, afforded the compounds **5a–5j**.

In the IR spectra, compounds **4a–4j** display two $\tilde{\nu}$(NH) bands in the 3 240–3 400 cm^{-1} region assigned to the intramolecularly bonded NH groups. The $\tilde{\nu}_s(NH_2)$ and $\tilde{\nu}_{as}(NH_2)$ bands of compounds **5a–5j** are observed in the 3 370–3 500 cm^{-1} region. The $\tilde{\nu}$(C=O) bands of carbonyl groups of the 2*H*-pyridazin-3-one ring are overlapped by the

$\tilde{\nu}$(C=N) and $\tilde{\nu}$(C=C) bands owing to the very high absorption coefficients of the bands at 1 610 cm^{-1}. Also, the similar situation being observed in the spectra of compounds **5a–5j**, only the $\tilde{\nu}$(C=O) bands are shifted to higher wavenumbers.

Chemical shifts of the N–H protons of compounds **5f–5j** having cyclic substituents



1, $R^1 = NH_2$
2, $R^1 = CH_3CONH$
3, $R^1 = (CH_3CO)_2N$

4a-4j

5a-5j

4, 5	R^2	R^3
a	CH_3	CH_3
b	C_2H_5	C_2H_5
c	C_3H_7	C_3H_7
d	C_2H_5	C_4H_9
e	i-C_4H_9	i-C_4H_9
f	$-C_4H_8-$	
g	$-C_5H_{10}-$	
h	$-C_6H_{12}-$	
i	$-C_7H_{14}-$	
j	$-(CH_2)_2O(CH_2)_2-$	

SCHEME 1

with except for **5j** are observed at lower values than those of compounds **5a–5e**, which can be explained by steric effects. The highest chemical shift of the N–H proton in compound **5j** can be explained by the *–I* efect of the morpholine oxygen atom. Chemical shifts of α-protons of both ethyl and butyl groups overlap. Chemical shifts of the C-5 and C-6 carbons increase with the ring enlargement. Chemical shifts of the C-4 and C-6 carbons are observed at higher values than those of compounds **4a–4j** whilst chemical shifts of C-5 move in opposite direction. In the pesticide screening none of the prepared compounds was as active as the standard used.

EXPERIMENTAL

Melting points were determined on Kofler apparatus and are uncorrected. All the compounds were checked for the purity by TLC on Silufol UV 254 plates (Lachema Brno, Czech Republic) in the system toluene–acetone 95 : 5 (v/v). Detection was carried out by UV-irradiation. Column chromatography was performed on silica gel (Lachema Brno, Czech Republic). The IR spectra, ($\tilde{\nu}$, cm^{-1}) were recorded on an FTIR PU 9802/25 (Phillips) spectrophotometer in chloroform (c 10^{-2} mol dm^{-3}, cell thickness 0.1 mm). UV spectra (λ, nm; log ε) were obtained with the M-40 spectrophotometer (Zeiss

TABLE I
Characteristic data for compounds **4a–4j** and **5a–5j**

Compound	M.p., °C Yield, %	Formula M.w.	Calculated/Found		
			% C	% H	% N
4a	206–207	$C_{14}H_{16}N_4O_2$	61.75	5.92	20.57
	83	272.2	61.89	6.14	20.71
4b	166–167	$C_{16}H_{20}N_4O_2$	63.99	6.71	18.66
	78	300.3	64.21	6.80	19.01
4c	148–150	$C_{18}H_{24}N_4O_2$	65.86	7.31	17.36
	81	328.2	65.98	7.31	17.26
4d	136–137	$C_{18}H_{24}N_4O_2$	65.86	7.31	17.36
	69	328.2	65.98	7.35	17.18
4e	162–163	$C_{20}H_{28}N_4O_2$	67.42	7.86	15.72
	87	356.3	67.28	8.16	15.82
4f	211–212	$C_{16}H_{18}N_4O_2$	64.45	6.04	18.78
	89	298.1	64.21	5.90	18.82
4g	172–173	$C_{17}H_{20}N_4O_2$	65.39	6.41	17.94
	90	312.2	65.49	6.52	17.86
4h	157–159	$C_{18}H_{22}N_4O_2$	66.28	7.74	17.17
	72	326.2	66.20	7.98	17.27
4i	178–179	$C_{19}H_{24}N_4O_2$	67.08	7.05	16.46
	81	340.2	67.23	7.02	16.57
4j	205–206	$C_{16}H_{18}N_4O_2$	61.15	5.73	17.82
	80	314.2	61.04	5.74	17.64
5a	151–155	$C_{12}H_{14}N_4O$	62.59	6.08	24.32
	80	230.3	62.70	6.19	24.41
5b	86–87	$C_{14}H_{18}N_4O$	65.13	6.97	21.69
	65	258.2	65.26	7.19	21.58
5c	89–92	$C_{16}H_{22}N_4O$	67.12	7.68	19.56
	68	286.3	67.31	7.82	19.53
5d	89–90	$C_{16}H_{22}N_4O$	67.12	7.68	19.56
	59	286.3	67.25	7.81	19.69
5e	68–70	$C_{18}H_{26}N_4O$	68.80	8.27	17.82
	77	314.2	68.31	8.38	18.10

TABLE I
(*Continued*)

Compound	M.p., °C Yield, %	Formula M.w.	Calculated/Found		
			% C	% H	% N
5f	150–152	$C_{14}H_{16}N_4O$	65.62	6.25	21.86
	77	256.2	65.71	6.21	21.98
5g	172	$C_{15}H_{18}N_4O$	66.66	6.66	20.72
	73	270.2	66.80	6.90	21.00
5h	122–123	$C_{16}H_{20}N_4O$	67.62	7.03	19.70
	67	284.2	67.44	7.08	19.64
5i	95–96	$C_{17}H_{22}N_4O$	68.46	7.37	18.78
	71	298.2	68.51	7.38	18.89
5j	219–220	$C_{14}H_{16}N_4O_2$	61.77	5.88	20.57
	63	272.2	61.64	5.74	20.41

Jena, Germany) in methanol (c 10^{-4} mol dm^{-3}, cell thickness 0.2 cm). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 (^{1}H) and 75 (^{13}C) MHz in hexadeuteriodimethyl sulfoxide with tetramethylsilane as internal standard. Chemical shifts are given in ppm (δ-scale), coupling constants and width of multiplets in Hz. Mass spectra were recorded on an MS 902 S spectrometer (70 eV) (A.E.I. Manchester, England).

Contact and systemic insecticidal activity was followed on *Calandra granaria*, *Musca domestica*, *Aphis fabae* using Malathion and Fenitrothion as standards, acaricidal and ovicidal activity on *Tetranychus urticae*, fungicidal activity was followed by the *in vitro* metod on fungi: *Tilletia foetida*, *Botrytis cinerea*, F*usarium avenaceum*, *Alternaria alternata* and by the *in vivo* mehtod on *Erysiphe graminis* and *Phytophtora infestans* according to the published methods[16,17], herbicidal activity with the preemergent application on *Avena fatua*, *Echinochloa cruss-gallii*, *Panicum miliaceum*, *Fagopyrum vulgare*, *Sinapis alba*, *Lepidium sativum* and *Beta vulgaris* according to described methods[18].

4-Acetylamino-5-chloro-2-phenyl-2*H*-pyridazin-3-one (**2**)

To acetyl chloride (200 cm^3) 4-amino-5-chloro-2-phenyl-2*H*-pyridazin-3-one (**1**; 49.8 g, 0.225 mol) was added and the reaction mixture was stirred under reflux 5 h. After cooling of the reaction mixture to 0 °C, the solid portion was isolated and recrystallized from ethanol; 42.3 g (71 %) of the compound **2**, m.p. 176–180 °C, was obtained. IR spectrum: 1 725 (CH_3CO), 1 625 (C=O + C=N), 3 275 (NH). UV spectrum (MeOH): 203 (4.52), 270 (3.69). ^{1}H NMR spectrum: 2.11 s, 3 H (CH_3CO), 8.43 s, 1 H (CH=N). ^{13}C NMR spectrum: 167.37 (CH_3**C**O), 157.36 (CO), 124.88 (C-4), 140.73 (C-5), 133.84 (C-6), 138.91 (C-1′), 125.27 (C-2′,6′), 129.03 (C-3′,5′), 128.51 (C-4′), 23.65 (**C**H_3CO). Mass spectrum, m/z: 263 ($M^{+\bullet}$), 221 ($M^{+\bullet}$ – CH_2CO). For $C_{12}H_{10}ClN_3O_2$ (263.7) calculated: 54.66% C, 3.82% H, 13.44% Cl, 15.94% N; found: 54.51% C, 3.88% H, 13.51% Cl, 16.01% N.

4-Diacetylamino-5-chloro-2-phenyl-2*H*-pyridazin-3-one (**3**)

To acetic anhydride (600 cm^3) 4-amino-5-chloro-2-phenyl-2*H*-pyridazin-3-one (**1**; 49.8 g, 0.225 mol) was added with stirring. The reaction mixture was stirred at reflux for 12 h. Acetic anhydride was destilled off under reduced pressure, and the residue was purified by crystallization from toluene giving a crystalline compound (40.2 g, m.p. 97–99 °C), which was repurified by column chromatography on silica gel using toluene–acetone 95 : 5 (v/v) as eluent to yield compound **3** (35.1 g, 51%) as white crystals, m.p. 100.7 °C. IR spectrum: 1 740 (CH_3CO), 1 615 (C=O + C=N). UV spectrum (MeOH): 265 (3.68), 318 (3.95). ^{1}H NMR spectrum: 2.39 s, 6 H (CH_3CO), 8.01 s, 1 H (CH=N). ^{13}C NMR

TABLE II
IR and UV spectral data of compounds **4a–4j** and **5a–5j**

Compound	IR spectrum			UV spectrum
	$\tilde{\nu}$(C=O)	$\tilde{\nu}$(NH)[a]	$\tilde{\nu}$(CH_3C=O)	λ_{max}(log ε)
4a	1 612	3 246, 3 381	1 689	249(3.39), 308(3.06)
4b	1 612	3 238, 3 377	1 689	241(3.42), 308(3.06)
4c	1 612	3 238, 3 375	1 689	247(3.45), 310(3.17)
4d	1 612	3 236, 3 375	1 691	247(3.43), 310(3.12)
4e	1 614	3 248, 3 381	1 691	243(3.38), 306(3.09)
4f	1 612	3 236, 3 389	1 687	245(2.78), 309(2.39)
4g	1 614	3 248, 3 381	1 691	251(3.41), 313(3.13)
4h	1 612	3 240, 3 379	1 687	247(3.43), 310(2.90)
4i	1 162	3 244, 3 357	1 687	248(3.34), 310(3.02)
4j	1 618	3 179, 3 373	1 695	247(3.17), 311(2.92)
5a	1 635	3 379, 3 489	–	253(3.32), 333(2.82)
5b	1 639	3 383, 3 499	–	256(3.18), 333(2.69)
5c	1 637	3 385, 3 499	–	257(3.19), 333(2.69)
5d	1 637	3 385, 3 499	–	257(3.22), 333(2.75)
5e	1 637	3 387, 3 503	–	258(3.13), 333(2.63)
5f	1 626	3 375, 3 487	–	245(3.42), 309(3.05)
5g	1 630	3 373, 3 485	–	254(3.33), 333(2.90)
5h	1 629	3 391, 3487	–	257(3.29), 333(2.78)
5i	1 631	3 383, 3 497	–	248(3.34), 333(2.88)
5j	1 641	3 379, 3 497	–	250(3.22), 333(2.68)

[a] $\tilde{\nu}_s$ (NH_2) and $\tilde{\nu}_{as}$ (NH_2) for compounds **5a–5j**.

TABLE III
^{1}H NMR spectra of the non-phenylic moiety of compounds **4a–4j** and **5a–5j**

Compound	^{1}H NMR spectrum
4a	2.00 s, 3 H (CH_3CO); 2.85 s, 6 H (CH_3); 8.01 s, 1 H (CH=N); 9.12 s, 1 H (NH)
4b	1.21 t, 6 H ($C\mathbf{H}_3CH_2$); 1.97 s, 3 H (CH_3CO); 3.35 q, 4 H ($CH_3C\mathbf{H}_2$); 7.95 s, 1 H (CH=N); 9.02 s, 1 H (NH)
4c	0.84 t, 6 H (CH_3); 1.54 m, 4 H (CH_2-β); 1.98 s, 3 H (CH_3CO); 3.29 t, 4 H (CH_2-α); 7.98 s, 1 H (CH=N); 9.08 s, 1 H (NH)
4d	0.87 t, 3 H (CH_3); 1.09 t, 3 H ($C\mathbf{H}_3CH_2N$); 1.32 sext. 2 H (CH_2-γ); 1.52 quin. 2 H (CH_2-β); 1.97 s, 3 H (CH_3CO); 3.30 m, 4 H (CH_2-α); 7.96 s, 1 H (CH=N); 9.07 s, 1 H (NH)
4e	0.80 d, 12 H (CH_3); 1.78 sext. 2 H (CH); 2.00 s, 3 H (CH_3CO); 3.22 d, 4 H (CH_2); 8.09 s, 1 H (CH=N); 9.15 s, 1 H (NH)
4f	1.84 m, 4 H (CH_2-β); 1.96 s, 3 H (CH_3CO); 3.47 t, 4 H (CH_2-α); 7.91 s, 1 H (CH=N); 8.97 s, 1 H (NH)
4g	1.55–1.50 m, 6 H (CH_2-β + CH_2-γ); 2.01 s, 3 H (CH_3CO); 3.31 t, 4 H (CH_2-α); 8.01 s, 1 H (CH=N); 9.17 s, 1 H (NH)
4h	1.49 m, 4 H (CH_2-γ); 1.72 m, 4 H (CH_2-β); 1.98 s, 3 H (CH_3CO); 3.54 t, 4 H (CH_2-α); 8.00 s, 1 H (CH=N); 9.15 s, 1 H (NH)
4i	1.52–1.50 m, 6 H (CH_2-γ + CH_2-δ); 1.63 m, 4 H (CH_2-β); 1.98 s, 3 H (CH_3CO); 3.53 t, 4 H (CH_2-α); 8.01 s, 1 H (CH=N); 9.21 s, 1 H (NH)
4j	2.02 s, 3 H (CH_3CO); 3.05 t, 4 H (CH_2-α); 3.79 t, 4 H (CH_2-β); 8.05 s, 1 H (CH=N); 9.48 s, 1 H (NH)
5a	2.67 s, 6 H (CH_3); 5.79 s, 2 H (NH_2); 7.85 s, 1 H (CH=N)
5b	0.98 t, 6 H (CH_3); 2.99 q, 4 H (CH_2); 5.76 s, 2 H (NH_2); 7.82 s, 1 H (CH=N)
5c	0.84 t, 6 H (CH_3); 1.40 m, 4 H (CH_2-β); 2.91 t, 4 H (CH_2-α); 5.73 s, 2 H (NH_2); 7.84 s, 1 H (CH=N)
5d	0.86 t, 3 H (CH_3-butyl); 0.99 t, 3 H (CH_3-ethyl); 1.12 t, 2 H (CH_2-γ); 1.30 m, 2 H (CH_2-β); 2.97 m, 4 H (CH_2-α); 5.70 s, 2 H (NH_2); 7.83 s, 1 H (CH=N)
5e	0.86 d, 12 H (CH_3); 1.71 m, 2 H (CH); 3.22 t, 4 H (CH_2); 5.58 s, 2 H (NH_2); 7.91 s, 1 H (CH=N)
5f	1.85 t, 4 H (CH_2-β); 3.26 t, 4 H (CH_2-α); 5.34 s, 2 H (NH_2); 7.81 s, 1 H (C=N)
5g	1.68 m, 2 H (CH_2-γ); 1.70 m, 4 H (CH_2-β); 3.17 t, 4 H (CH_2-α); 5.29 s, 2 H (NH_2); 7.91 s, 1 H (CH=N)
5h	1.69 m, 4 H (CH_2-γ); 1.71 m, 4 H (CH_2-β); 3.18 t, 4 H (CH_2-α); 5.47 s, 2 H (NH_2); 7.84 s, 1 H (CH=N)
5i	1.52–1.50 m, 6 H (CH_2-(γ + δ)); 1.63 m, 4 H (CH_2-β); 3.28 t, 4 H (CH_2-α); 5.35 s, 2 H (NH_2); 7.87 s, 1 H (CH=N)
5j	2.92 t, 4 H (CH_2-α); 3.75 t, (CH_2-β); 5.93 s, 2 H (NH_2); 7.86 s, 1 H (C=N)

TABLE IV
^{13}C NMR spectra of the compounds **4a–4j** and **5a–5j**

Compound	^{13}C NMR spectrum
4a	22.6 (CO**C**H$_3$), 40.3 (CH$_3$N), 127.3 (C-4′), 128.8 (C-3′,5′), 125.3 (C-2′,6′), 141.7 (C-1′), 110.6 (C-4), 144.7 (C-5), 138.4 (C-6), 158.7 (C=O), 168.6 (CH$_3$**C**O)
4b	13.8 (CH$_3$), 22.5 (CO**C**H$_3$), 44.5 (CH$_2$), 127.2 (C-4′), 128.4 (C-3′,5′), 125.2 (C-2′,6′), 141.7 (C-1′), 110.7 (C-4), 143.4 (C-5), 132.2 (C-6), 158.8 (C=O), 169.0 (CH$_3$**C**O)
4c	10.9 (CH$_3$), 21.5 (CH$_2$-β), 22.5 (CO**C**H$_3$), 52.4 (CH$_2$-α), 127.2 (C-4′), 128.4 (C-3′,5′), 125.1 (C-2′,6′), 141.7 (C-1′), 110.5 (C-4), 143.2 (C-5), 132.2 (C-6), 158.7 (C=O), 169.3 (CH$_3$**C**O)
4d	13.8 (CH$_3$), 19.5 (CH$_2$-γ), 22.5 (CO**C**H$_3$), 30.4 (CH$_2$-βbutyl), 45.4 (CH$_2$-αethyl), 49.9 (CH$_2$-αbutyl), 127.2 (C-4′), 128.0 (C-3′,5′), 125.2 (C-2′,6′), 141.6 (C-1′), 110.5 (C-4), 143.3 (C-5), 132.0 (C-6), 158.8 (C=O), 169.3 (CH$_3$**C**O)
4e	19.7 (CH$_3$), 22.4 (CO**C**H$_3$), 27.3 (CH), 59.6 (CH$_2$), 127.2 (C-4′), 128.4 (C-3′,5′), 125.1 (C-2′,6′), 141.6 (C-1′), 111.3 (C-4), 143.4 (C-5), 132.7 (C-6), 158.6 (C=O), 169.0 (CH$_3$**C**O)
4f	22.5 (CO**C**H$_3$), 24.9 (CH$_2$-β), 48.8 (CH$_2$-α), 127.1 (C-4′), 128.4 (C-3′,5′), 125.2 (C-2′,6′), 141.8 (C-1′), 108.2 (C-4), 142.2 (C-5), 131.6 (C-6), 158.9 (C=O), 169.6 (CH$_3$**C**O)
4g	22.5 (CO**C**H$_3$), 23.7 (CH$_2$-γ), 25.7 (CH$_2$-β), 48.2 (CH$_2$-α), 127.3 (C-4′), 128.5 (C-3′,5′), 125.3 (C-2′,6′), 141.6 (C-1′), 113.7 (C-4), 144.5 (C-5), 134.1 (C-6), 158.7 (C=O), 168.1 (CH$_3$**C**O)
4h	22.5 (CO**C**H$_3$), 26.2 (CH$_2$-γ), 28.1 (CH$_2$-β), 50.5 (CH$_2$-α), 127.2 (C-4′), 128.4 (C-3′,5′), 125.2 (C-2′,6′), 141.7 (C-1′), 109.7 (C-4), 144.0 (C-5), 131.8 (C-6), 158.9 (C=O), 169.1 (CH$_3$**C**O)
4i	22.5 (CO**C**H$_3$), 23.9 (CH$_2$-γ), 26.6 (CH$_2$-β), 26.8 (CH$_2$-δ), 51.6 (CH$_2$-α), 127.2 (C-4′), 128.4 (C-3′,5′), 125.1 (C-2′,6′), 141.6 (C-1′), 109.8 (C-4), 143.0 (C-5), 131.8 (C-6), 158.8 (C=O), 169.3 (CH$_3$**C**O)
4j	22.5 (CO**C**H$_3$), 47.4 (CH$_2$-α), 63.2 (CH$_2$-β), 127.5 (C-4′), 128.5 (C-3′,5′), 125.4 (C-2′,6′), 141.6 (C-1′), 114.7 (C-4), 143.8 (C-5), 131.8 (C-6), 158.8 (C=O), 168.3 (CH$_3$**C**O)
5a	41.2 (CH$_3$N), 125.7 (C-2′,6′), 127.4 (C-4′), 128.4 (C-3′,5′), 142.1 (C-1′), 128.2 (C-4), 134.6 (C-5), 133.7 (C-6), 156.2 (C=O)
5b	12.6 (CH$_3$), 45.2 (CH$_2$), 125.6 (C-2′,6′), 127.3 (C-4′), 128.4 (C-3′,5′), 142.1 (C-1′), 124.6 (C-4), 138.7 (C-5), 136.2 (C-6), 156.3 (C=O)
5c	11.5 (CH$_3$), 20.3 (CH$_2$-β), 53.2 (CH$_2$-α), 125.6 (C-2′6′), 127.4 (C-4′), 128.4 (C-3′,5′), 142.1 (C-1′), 125.2 (C-4), 137.9 (C-5), 136.3 (C-6), 156.3 (C=O)
5d	13.7 (CH$_3$ethyl, butyl), 19.7 (CH$_2$-γ), 29.3 (CH$_2$-β), 45.6 (CH$_2$-αbutyl), 125.5 (C-2′,6′), 127.3 (C-4′), 128.3 (C-3′,5′), 142.2 (C-1′), 124.8 (C-4), 138.3 (C-5), 136.2 (C-6), 156.2 (C=O)
5e	20.5 (CH$_3$), 26.5 (CH), 59.4 (CH$_2$), 125.6 (C-2′,6′), 127.4 (C-4′), 128.4 (C-3′,5′), 142.1 (C-1′), 126.4 (C-4), 138.5 (C-5), 136.4 (C-6), 156.3 (C=O)
5f	24.3 (CH$_2$-β), 48.6 (CH$_2$-α), 125.5 (C-2′,6′), 127.3 (C-4′), 128.4 (C-3′,5′), 142.2 (C-1′), 127.6 (C-4),130.1 (C-5), 132.5 (C-6), 156.4 (C=O)
5g	25.9 (CH$_2$-γ), 29.1 (CH$_2$-β), 51.1 (CH$_2$-α), 125.5 (C-2′,6′), 127.3 (C-4′), 128.4 (3′,5′), 142.0 (C-1′), 128.1 (C-4), 132.1 (C-5), 135.1 (C-6), 156.3 (C=O)

TABLE IV
(*Continued*)

Compound	^{13}C NMR spectrum
5h	26.8 (CH_2-γ), 28.8 (CH_2-β), 51.9 (CH_2-α), 125.5 (C-2′,6′), 127.4 (C-4′), 128.4 (3′,5′), 142.0 (C-1′), 129.5 (C-4), 133.9 (C-5), 135.4 (C-6), 156.4 (C=O)
5i	24.7 (CH_2-γ), 26.9 (CH_2-δ), 27.6 (CH_2-β), 50.9 (CH_2-α), 125.4 (C-2′,6′), 127.3 (C-4′), 128.3 (3′,5′), 141.9 (C-1′), 128.7 (C-4), 133.6 (C-5), 136.0 (C-6), 156.5 (C=O)
5j	49.2 (CH_2-α), 66.3 (CH_2-β), 125.7 (C-2′,6′), 127.5 (C-4′), 128.5 (C-3′,5′), 142.1 (C-1′), 126.4 (C-4), 135.8 (C-5), 133.8 (C-6), 156.3 (C=O)

spectrum: 170.49 (CH_3**C**O), 156.84 (CO), 118.25 (C-4), 140.47 (C-5), 136.57 (C-6), 140.21 (C-1′), 124.88 (C-2′,6′), 128.90 (C-3′,5′), 127.32 (C-4′), 25.43 (**C**H_3CO). Mass spectrum, *m/z*: 305 ($M^{\ddagger}$), 263 ($M^{\ddagger}$ – CH_2CO), 77 ($C_6H_5^{\ddagger}$). For $C_{14}H_{12}ClN_3O_3$ (305.7) calculated: 55.00% C, 3.96% H, 11.60% Cl, 13.75% N; found: 55.10% C, 3.99% H, 11.71% Cl, 13.81% N.

General Procedure for Preparation of 4-Acetylamino-5-(disubstituted amino)-2-phenyl-2*H*-pyridazin-3-ones **4b–4j**

Procedure A. To 4-diacetylamino-5-chloro-2-phenyl-2*H*-pyridazin-3-one (**3**; 6.1 g, 0.02 mol)) in toluene (80 cm^3) an appropriate secondary or cyclic amine (0.04 mol) excepting dimethylamine, was added with stirring and the reaction mixture was stirred at boiling temperature for 3 h. After cooling the solid portion was filtered off, triturated with water, dried, and the residue was chromatographed on a column of silica gel (200 g). By TLC it was found that two compounds were formed which were separated by elution with toluene containing acetone (10 g per 100 cm^3). A side product was found to be 4-acetylamino-5-chloro-2-phenyl-2*H*-pyridazin-3-one **2**. The characteristic data, infrared and UV spectra of the compounds **4** are given in Tables I and II, their NMR spectra in Tables III and IV.

Procedure B. To 4-acetylamino-5-chloro-2-phenyl-2*H*-pyridazin-3-one (**2**; 5.2 g, 0.02 mol) in toluene (80 cm^3) an appropriate amine (0.04 mol) excepting dimethylamine, was added with stirring for 4 h. The raw products were collected by filtration, washed with water, dried and purified by crystallization from ethanol.

4-Acetylamino-5-dimethylamino-2-phenyl-2*H*-pyridazin-3-one (**4a**)

Dimethylamine (1.8 g, 0.04 mol) cooled to 0 °C was added to 4-acetylamino-5-chloro-2-phenyl-2*H*-pyridazin-3-one (**2**; 5.2 g, 0.02 mol) in toluene (80 cm^3) with stirring. The reaction mixture was then heated in autoclave at 150 °C for 6 h. After cooling to 10 °C, the solid portion was filtered off, triturated with water dried and recrystallized from ethanol. Its characteristic data, infrared and UV spectra are given in Tables I and II, NMR spectra in Tables III and IV.

General Procedure for Preparation of 4-Amino-5-(disubstituted amino)-2-phenyl-2*H*-pyridazin-3-ones **5a–5j**

To sodium ethanolate prepared from ethanol (30 cm^3) and sodium (0.2 g) the 4-acetylamino derivatives **4a–4j** (0.01 mol) were added and the reaction mixture was refluxed 4 h and then slowly cooled to room temperature with stirring. Ethanol was distilled off under reduced pressure. Crystallization of the residues from a suitable solvent yielded the corresponding amino derivatives **5a–5j**. Their characteristic data, infrared and UV spectra are given in Tables I and II, their NMR spectra in Tables III and IV.

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