Chemistry of Heterocyclic Compounds, Vol. 39, No. 9, 2003

SYNTHESIS OF DERIVATIVES OF 1-(9-ALKYL-9H-CARBAZOL-3-YL)-4-CARBOXY-2-PYRROLIDINONES

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Derivatives of 1-(9-alkyl-9H-carbazol-3-yl)-4-carboxy-2-pyrrolidinones (methyl esters, hydrazides) were synthesized. The condensation of the synthesized hydrazides with aromatic aldehydes, acetylacetone, and acetoacetic ester was studied. Structure of the obtained compounds was confirmed by IR and NMR spectroscopy. The specific characteristics of the substituents are discussed.

Keywords: 1-(9-alkyl-9H-carbazol-3-yl)-4-carboxy-2-pyrrolidinones, arylidenehydrazides, 3,5-dimethylpyrazoles, condensation, NMR spectra, cyclization.

The interest in the chemistry of carbazole is due to the extensive use of its derivatives in the production of photosemiconductors [1-3]. Fragments of carbazole are also present in certain alkaloids [4-6]. In the present work we have synthesized new derivatives of 9-alkylcarbazoles containing a 4-carboxy-2-pyrrolidine substituent. Derivatives of 4-carboxy-2-pyrrolidinone are plant growth regulators [7, 8] and are also used in the synthesis of pharmaceutical preparations [9, 10].

The structure of the synthesized compounds was investigated by IR and NMR spectroscopy. The signals in the ^{1}H NMR spectra were assigned on the basis of the characteristic chemical shifts of the respective structural fragments, the spin–spin coupling constants, and the integral intensities of the signals.

The synthesis of the initial 1-(9-alkyl-9H-carbazol-3-yl)-4-carboxy-2-pyrrolidinones **1** and **2** was described in [11]. 4-Carboxy-1-(9-propyl-9H-carbazol-3-yl)-2-pyrrolidinone (**3**) was synthesized by the same method from 3-amino-9-propylcarbazole and itaconic acid with a yield of 59%. By boiling compounds **1**-**3** in methanol in the presence of sulfuric acid we obtained the corresponding methyl esters **4**-**6**. In the ^{1}H NMR spectra of compounds **4**-**6** the resonance absorption of the hydrogen atoms of the carbazolyl fragment was observed in the region of 7.16-8.30 ppm. Unsymmetrical 4'-substitution of the pyrrolidinone ring gives rise to magnetic nonequivalence in the geminal protons of the $COCH_2$ and NCH_2 methylene groups, as a result of which characteristic multiplets were observed in the regions of 2.70-2.92 and 4.07-4.25 ppm, and a quintet for the CH group of the pyrrolidinone ring was observed at 3.52 ppm.

The respective carbohydrazides **7**-**9** were obtained heating methyl esters **4**-**6** with an excess of hydrazine hydrate. Unlike the corresponding spectra of compounds **4**-**6** the ^{1}H NMR spectra of compounds **7**-**9** do not show the absorption of the $COCH_3$ group at 3.71 ppm. The appearance of broadened two-proton (δ 4.21-4.32 ppm) and one-proton (δ 9.32-9.34 ppm) signals indicates the presence of the $CONHNH_2$ group. In the IR spectra of compounds **7**-**9**, in addition to strong νC=O absorption bands at 1603 and 1607 (**7**), 1648 and 1687 (**8**), and 1647 and 1687 cm^{-1} (**9**), there is a strong absorption band for the hydrazine fragment $CONHNH_2$ in the region of 3140-3425 cm^{-1}.

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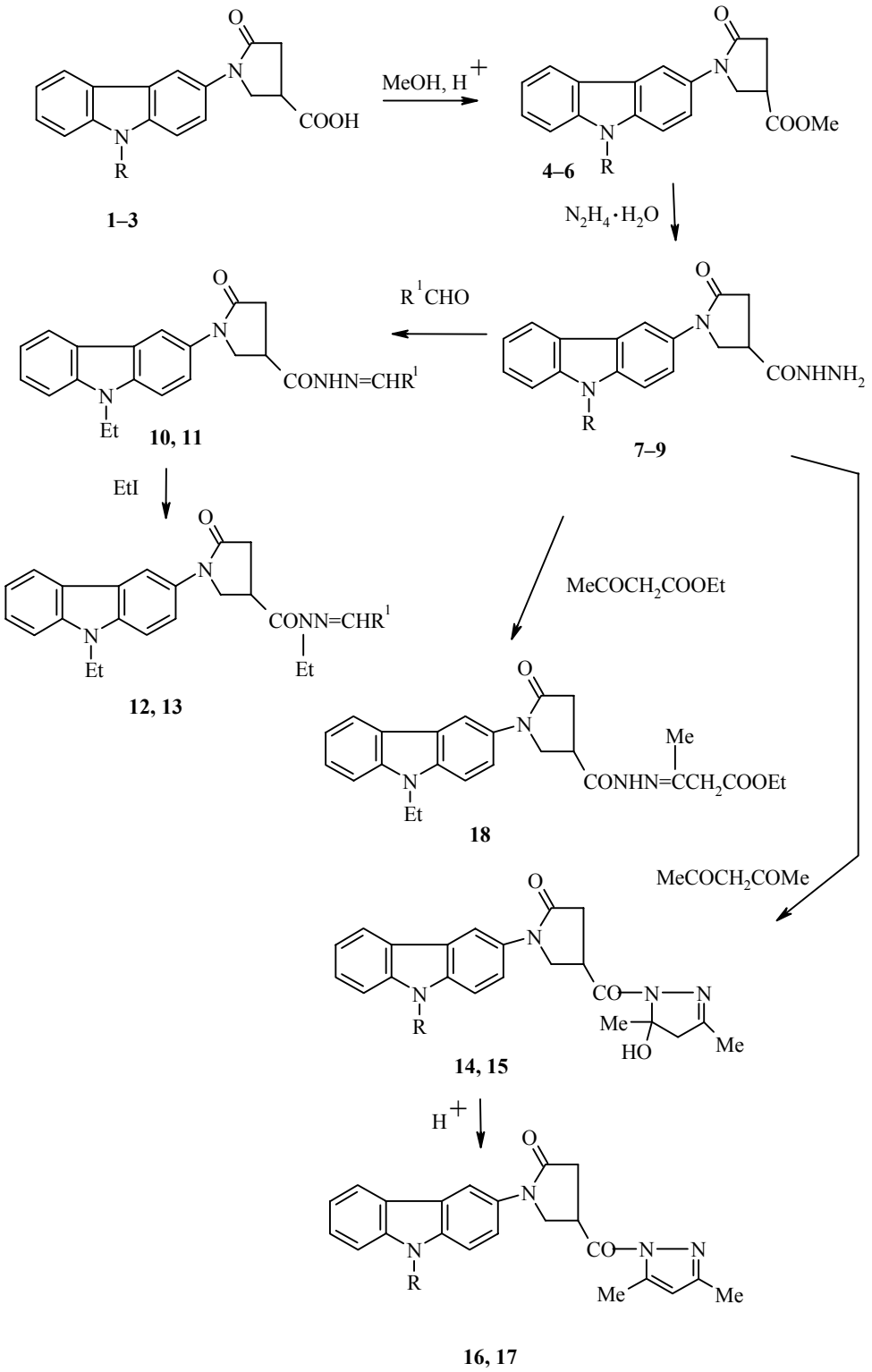


1, **4**, **7** R = Me; **2**, **5**, **8**, **14**, **16** R = Et; **3, 6**, **9**, **15, 17** R = *n*-Pr;
10, **12** R^1 = 4-$Et_2NC_6H_4$; **11**, **13** R^1 = 9-ethyl-9-carbazol-3-yl

The condensation of hydrazides **8** and **9** with carbonyl compounds was investigated. By heating hydrazide **8** with aromatic aldehydes the respective benzylidenehydrazides **10** and **11** were obtained. The ^{1}H NMR spectra of solutions of compounds **10** and **11** in deuterochloroform contain signals for the aromatic and N=CH protons in the region of 7.14-8.47 ppm and also downfield absorption for the proton of the CONH group, which was represented in deuterochloroform by a single one-proton signal and in DMSO solution by two broad signals at 11.50 and 11.57 ppm with an overall integral intensity of 1. It is necessary to mention that on account of the different positions of the substituents in relation to the double bond (the N=CH group) compounds **10** and **11** exist as mixtures of *Z*- and *E*-isomers.* From the intensity of the signals at 11.50 and 11.57 ppm it was concluded that compound **10** exists in the form of mixture of 41% of the *E*-isomer and 59% of the *Z*-isomer while compound **11** exists in the form of mixture of 37% of the *E*-isomer and 63% of the *Z*-isomer.

Compounds **10** and **11** were then subjected to alkylation with iodoethane in the presence of a mixture of potassium hydroxide and carbonate. The IR spectra of the alkylated compounds **12** and **13** do not contain absorption bands in the region characteristic of the NH group. In the ^{1}H NMR spectra, apart from the signals characteristic of the protons of compounds **10** and **11** there are signals for the protons of the CH_2CH_3 group. During investigation of the condensation of hydrazides **8** and **9** with acetylacetone at 20°C in methanol we were able to isolate and characterize the intermediate condensation products – derivatives of 5-hydroxy-3,5-dimethyl-4,5-dihydropyrazole **14** and **15**. A series of new signals that appear, such as singlets for the CH_3 groups [δ 1.82 and 2.05 (2.15) ppm], a singlet for the CH_2 group at 2.95 ppm, and a low-intensity broadened signal for the OH group at 5.22 (5.70) ppm, undoubtedly indicate the presence of compounds **14** and **15**.

Under the influence of acids or temperature the derivatives of 5-hydroxy-3,5-dimethyl-4,5-dihydropyrazole **14** and **15** undergo cyclization to 3,5-dimethylpyrazoles **16** and **17**. The formation of the pyrazole ring in compounds **16** and **17** was confirmed by the presence of a characteristic signal for the CH=N fragment at 6.01 and also two singlets for the CH_3 groups at 2.25 and 2.58 ppm.

During condensation of hydrazide **8** with acetoacetic ester in ethanol 3-substituted ethyl butanoate **18** was isolated. Its formation was confirmed by the presence of signals for the CH_3 (δ 1.99 ppm) and CH_2 (δ 3.32 ppm) groups and also by the characteristic triplet and quartet of the OCH_2CH_3 group at 1.40 and 4.15 ppm respectively. The presence of two broad signals for the CONH group with greater and lesser intensity at 9.20 and 9.65 ppm indicates that compound **18** exists in the form of mixture of 14% of the *E*-isomer and 86% of the *Z*-isomer.

Analysis of the more informative ^{13}C NMR spectra was complicated by the absence of increments for the effect of the pyrrolidone substituent on the carbazole carbon atoms. In order to establish the unknown increments we used the model compounds that we synthesized, the structure of which contained a *p*-substituted aromatic fragment (pyrrolidinonyl-C_6H_4–R). The type of substitution of the aromatic ring and the published increments [13] of the substituent (R = $COCHCHC_6H_5$) made it possible to calculate the influence of the pyrrolidinone substituent on the aromatic carbon atoms. By means of the obtained data (Δδ, ppm: C_i = 10.6, C_o = -11.92, C_m = -0.85, C_p = -5.63) we assigned the signals of the 1-1a carbazolyl carbon atoms in all the investigated compounds. On the basis of the assignment we refined the mean value of the increments of the pyrrolidinone substituent for the carbazole carbon atoms in this type of compounds (Δδ, ppm: C_i = 12.50, C_o = -6.77, C_m = -0.24, C_p = -2.90). In the ^{13}C NMR spectra of the synthesized compounds change of the N-substituent in the carbazolyl in the series CH_3, CH_2CH_3, $CH_2CH_2CH_3$ did not have a significant effect on the chemical shifts of the carbazolyl carbon atom.

By the INEPT procedure [14] it was possible to identify the resonance signals of the carbon atoms, and this made it possible to assign correctly the spectral lines both of the aromatic carbon atoms in the carbazolyl fragment and of the pyrrolidinone or pyrazole ring. The $CONHNH_2$ substituent of the pyrrolidinone ring in

* As a result of the stronger screening the spectral lines of the *Z*-isomers are observed in the upfield region [12].

TABLE 1. The Physicochemical Characteristics of the Synthesized Compounds **3-18**

Compound	Empirical formula	Found, % / Calculated, %			mp, °C*	IR spectrum, ν, cm^{-1}	Yield, %
		C	H	N			
1	2	3	4	5	6	7	8
3	$C_{20}H_{20}N_2O_3$	71.33 / 71.42	5.68 / 6.00	8.28 / 8.32	163-164		84.7
4	$C_{19}H_{18}N_2O_3$	70.45 / 70.80	6.01 / 5.63	8.34 / 8.69	114-115	1693 (CO); 1734 (CO)	61.0
5	$C_{20}H_{20}N_2O_3$	71.73 / 71.42	6.29 / 6.00	7.83 / 8.32	96-97	1688 (CO); 1741 (CO)	59.2
6	$C_{21}H_{22}N_2O_3$	71.75 / 71.98	6.47 / 6.32	7.51 / 7.99	92-93	1699 (CO); 1738 (CO)	44.0
7	$C_{18}H_{18}N_4O_2$	67.30 / 67.07	6.00 / 5.63	17.05 / 17.38	137-138	1603 (CO); 1670 (CO); 3282, 3418 (NH, NH_2)	75.2
8	$C_{19}H_{20}N_4O_2$	68.00 / 67.84	6.15 / 6.00	16.32 / 16.65	168-170	1648 (CO); 1687 (CO); 3289, 3425 (NH, NH_2)	80.0
9	$C_{20}H_{22}N_4O_2$	68.42 / 68.56	6.39 / 6.33	15.56 / 15.98	181-183	1647 (CO); 1687 (CO); 3140-3420 (NH, NH_2)	65.6
10	$C_{30}H_{33}N_5O_2$	72.49 / 72.70	6.42 / 6.72	14.36 / 14.13	127-128	1600 (CO); 1678 (CO); 3206 (NH)	60.0
11	$C_{34}H_{31}N_5O_2$	75.09 / 75.40	5.48 / 5.77	12.61 / 12.93	165 (decomp.)	1628 (CO); 1681 (CO); 3211 (NH)	33.7

TABLE 1 (continued)

1	2	3	4	5	6	7	8
12	$C_{32}H_{37}N_5O_2$	73.30 / 73.40	7.42 / 7.12	13.14 / 13.37	162-163	1664 (CO); 1695 (CO)	61.0
13	$C_{36}H_{35}N_5O_2$	76.20 / 75.90	5.62 / 6.20	12.26 / 12.29	212-213	1671 (CO); 1692 (CO)	55.8
14	$C_{24}H_{26}N_4O_3$	68.54 / 68.88	6.39 / 6.26	13.56 / 13.39	53 (decomp.)	3406 (OH); 1689 (CO); 1665 (CO)	64.0
15	$C_{25}H_{28}N_4O_3$	69.49 / 69.42	6.49 / 6.53	13.06 / 12.95	48 (decomp.)		62.0
16	$C_{24}H_{24}N_4O_2$	72.08 / 71.98	5.79 / 6.04	13.79 / 13.99	160-161.5	1693 (CO); 1724 (CO)	87.4
17	$C_{25}H_{26}N_4O_2$	72.49 / 72.44	6.08 / 6.32	13.62 / 13.52	138-139.5	1692 (CO); 1722 (CO)	50.8
18	$C_{25}H_{28}N_4O_4$	66.55 / 66.95	6.10 / 6.29	12.32 / 12.49	133-134	1691 (CO); 1734 (CO); 3248 (NH)	63.7

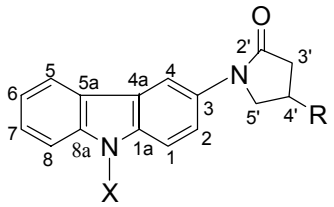
* Solvents: dioxane (compound **3**), acetone–hexane (compounds **4-6**, **12-15**, **18**), ethanol (compounds **7-9**), acetone–hexane–chloroform (compound **10**), dioxane–propane (compound **11**), and methanol (compounds **16** and **17**).

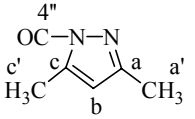
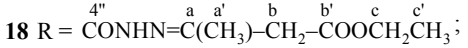
TABLE 2. The ^{1}H NMR Spectral Characteristics of the Synthesized Compounds **3-18***

Com-pound	Chemical shifts, δ, ppm (SSCC, *J*, Hz)
3	0.87 (3H, t, *J* = 7.1, $NCH_2CH_2\underline{CH_3}$); 1.80 (2H, m, $NCH_2\underline{CH_2}CH_3$); 2.70-2.92 (2H, m, $COCH_2$); 3.41 (1H, m, CH); 4.07-4.25 (2H, m, NCH_2); 4.35 (2H, m, $N\underline{CH_2}CH_2CH_3$); 7.13-8.33 (7H, m, H arom.)
4	2.70-2.92 (2H, m, $COCH_2$); 3.52 (1H, m, CH); 3.71 (3H, s, $COOCH_3$); 3.86 (3H, s, NCH_3); 4.07-4.25 (2H, m, NCH_2); 7.17-8.28 (7H, m, H arom.)
5	1.29 (3H, t, *J* = 7.05, $NCH_2\underline{CH_3}$); 2.70-2.95 (2H, m, $COCH_2$); 3.53 (1H, m, CH); 3.71 (3H, s, $COOCH_3$); 4.08-4.25 (2H, m, $N\underline{CH_2}$); 4.40 (2H, q, *J* = 7.05, $N\underline{CH_2}CH_3$); 7.17-8.30 (7H, m, H arom)
6	0.85 (3H, t, *J* = 7.36, $NCH_2CH_2\underline{CH_3}$); 1.78 (2H, m, $NCH_2\underline{CH_2}CH_3$); 2.79-2.85 (2H, m, $COCH_2$); 3.53 (1H, m, CH); 3.72 (3H, s, $COOCH_3$); 4.12-4.19 (2H, m, NCH_2); 4.34 (2H, t, *J* = 6.91, $N\underline{CH_2}CH_2CH_3$); 7.16-8.30 (7H, m, H arom.)
7	2.64-2.82 (2H, m, $COCH_2$); 3.25 (1H, m, CH); 3.86 (3H, s, NCH_3); 3.95-4.20 (2H, m, NCH_2); 4.32 (2H, s, NH_2); 7.10-8.55 (7H, m, H arom.); 9.32 (1H, s, CONH)
8	1.29 (3H, t, *J* = 7.0, $NCH_2\underline{CH_3}$); 2.63-2.87 (2H, m, $COCH_2$); 3.19-3.32 (1H, m, CH); 4.01-4.16 (2H, m, NCH_2); 4.21 (2H, s, NH_2); 4.40 (2H, q, *J* = 7.0, $N\underline{CH_2}CH_3$); 7.17-8.30 (7H, m, H arom.); 9.34 (1H, s, CONH)
9	0.85 (3H, t, *J* = 7.1, $NCH_2CH_2\underline{CH_3}$); 1.74-1.83 (2H, m, $NCH_2\underline{CH_2}CH_3$); 2.70-2.75 (2H, m, $COCH_2$); 3.19-3.32 (1H, m, CH); 3.97-4.13 (2H, m, NCH_2); 4.24 (2H, s, NH_2); 4.34 (2H, t, *J* = 7.1, $N\underline{CH_2}CH_2CH_3$); 7.16-8.29 (7H, m, H arom.); 9.34 (1H, s, CONH)
10*[2]	1.18 (6H, t, *J* = 7.03, $N(CH_2\underline{CH_3})_2$); 1.41 (3H, t, *J* = 7.18, $NCH_2\underline{CH_3}$); 2.95-3.26 (2H, m, $COCH_2$); 3.34-3.43 (4H, m, $N(\underline{CH_2}CH_3)_2$); 4.15-4.43 (5H, m, $N\underline{CH_2}CH_3 + NCH_2$+ CH); 7.15-8.35 (12H, m, H arom. + N=CH); 9.47 (1H, s, CONH) [1.15 (6H, m, $N(CH_2\underline{CH_3})_2$); 1.39 (m, $NCH_2\underline{CH_3}$); 2.70-2.90 (2H, m, $COCH_2$), in the range of ~3.5 ppm the signals are concealed by the signal of water, 6.64-8.40 (12H, m, H arom. + N=CH); 11.50 and 11.57 (1H, 2s, CONH)]. Mixture of *E*- and *Z*-isomers, 41/59%
11	1.27-1.34 (6H, m, $NCH_2\underline{CH_3} + NCH_2\underline{CH_3}$); 2.83-2.94 (2H, m, $COCH_2$); 3.50 (1H, m, CH); 4.15-4.48 (6H, m, $(N\underline{CH_2}CH_3) + NCH_2CH_3 + NCH_2$); 7.14-8.47 (15H, m, H arom. + N=CH); 11.50 and 11.57 (1H, 2s, CONH). Mixture of *E* and *Z* isomers, 37/63%
12	1.16-1.25 (9H, m, $N(CH_2\underline{CH_3})_2 + NCH_2\underline{CH_3}$); 1.41 (3H, t, *J* = 7.18, $NCH_2\underline{CH_3}$); 2.90-3.25 (2H, m, $COCH_2$); 3.38 (4H, q, *J* = 7.03, $N(\underline{CH_2}CH_3)_2$); 4.15-4.46 (7H, m, $2N\underline{CH_2}CH_3 + NCH_2$ + CH); 7.15-8.30 (12H, m, H arom. + N=CH)
13	1.29, 1.40, 1.44 (9H, 3t, *J* = 7.10, *J* = 4.93, *J* = 4.93, $3NCH_2\underline{CH_3}$); 3.00-3.28 (2H, m, $COCH_2$); 4.15-4.60 (9H, m, $3N\underline{CH_2}CH_3 + NCH_2$ + CH); 7.15-8.40 (15H, m, H arom. + N = CH)
14	1.32 (3H, t, *J* = 7.1, $NCH_2\underline{CH_3}$); 1.82 (3H, s, CH_3); 2.05 (3H, s, CH_3); 2.69-2.88 (2H, m, $COCH_2$); 2.95 (2H, s, CH_2); 3.88-4.22 (3H, m, NCH_2 + CH); 4.40 (2H, q, *J* = 7.1, $N\underline{CH_2}CH_3$); 5.22 (1H, s, OH); 7.09-8.38 (7H, m, H arom.)
15	0.95 (3H, t, *J* = 7.1, $NCH_2CH_2\underline{CH_3}$); 1.82 (3H, s, CH_3); 2.15 (3H, s, CH_3); 2.40-2.66 (2H, m, $NCH_2\underline{CH_2}CH_3$); 2.68-2.93 (2H, m, $COCH_2$); 2.95 (2H, s, CH_2); 3.85-4.28 (3H, m, NCH_2 + CH); 4.38 (2H, t, *J* = 7.1, $N\underline{CH_2}CH_2CH_3$); 5.70 (1H, s, OH); 7.06-8.40 (7H, m, H arom.)
16	1.41 (3H, t, *J* = 7.1, $NCH_2\underline{CH_3}$); 2.25 (3H, s, CH_3); 2.58 (3H, s, CH_3); 3.00-3.19 (2H, m, $COCH_2$); 4.23-4.37 (4H, m, $N\underline{CH_2}CH_3 + NCH_2$); 4.63 (1H, m, CH); 6.01 (1H, s, CH); 7.20-8.18 (7H, m, H arom.)
17	0.95 (3H, t, *J* = 7.1, $NCH_2CH_2\underline{CH_3}$); 1.89 (2H, m, $NCH_2\underline{CH_2}CH_3$); 2.25 (3H, s, CH_3); 2.58 (3H, s, CH_3); 3.00-3.19 (2H, m, $COCH_2$); 4.23-4.37 (4H, m, $N\underline{CH_2}CH_2CH_3 + NCH_2$); 4.63 (1H, m, CH); 6.02 (1H, s, CH); 7.20-8.17 (7H, m, H arom.)
18	1.26 (3H, t, *J* = 7.0, $NCH_2\underline{CH_3}$); 1.40 (3H, t, *J* = 7.2, $COOCH_2\underline{CH_3}$); 1.99 (3H, s, CH_3); 2.87-3.10 (2H, m, $COCH_2$); 3.32 (2H, s, $\underline{CH_2}COOC_2H_5$); 4.07-4.27 (5H, m, $NCH_2 + COO\underline{CH_2}CH_3$ + CH); 4.35 (2H, q, *J* = 7.0, $N\underline{CH_2}CH_3$); 7.20-8.17 (7H, m, H arom.); 9.20 and 9.65 (1H, 2s, CONH). Mixture of *E*- and *Z*-isomers, 14/86%

* The ^{1}H NMR spectra were recorded in DMSO-d_6 (compounds **3-9**, **11**), $CDCl_3$ (compounds **10**, **12**, **13**, **16-18**), and acetone (compounds **14** and **15**).
*[2] The data from the ^{1}H NMR spectra recorded in DMSO-d_6 are given in brackets.

TABLE 3. The ^{13}C NMR Spectral Characteristics of Compounds **4-9**, **16**, and **18**



3 R = COOH, **4**–**6** R = $COOCH_3$, **7-9** R = $CONHNH_2$; **16** R =  , **18** R =  ;

3, **6**, **9** X = C_3H_7, **4**, **7** X = CH_3, **5**, **8** X = C_2H_5, **16**, **18** X = C_2H_5

Atom C	Chemical shifts (DMSO-d_6), δ, ppm									
	3	**4**	**5**	**5***	**6**	**7**	**8**	**9**	**16***	**18***
1	2	3	4	5	6	7	8	9	10	11
C-1	109.06	108.62	108.84	108.08	109.07	108.83	108.82	109.05	108.60	108.56
C-2	119.49	119.44	119.56	120.16	119.52	119.38	119.51	119.47	120.33	120.24
C-3	131.07	131.06	131.01	130.37	130.95	131.19	131.15	131,09	130.56	130.71
C-4	112.51	112.43	112.66	113.70	112.55	112.56	112.56	112.46	113.90	113.69
C-4a	121.71	121.43	121.89	122.68	121.72	121.64	121.87	121.69	122.76	122.74
C-1a	137.25	137.79	136.71	137.71	137.29	137.70	136.64	137.22	137.73	137.62
C-5a	121.87	121.83	122.03	122.96	121.87	121.82	122.02	121.85	122.99	122.94
C-5	120.33	120.25	120.41	120.64	120.33	120.22	120.39	120.30	120.65	120.63
C-6	118.54	118.62	118.61	118.89	118.56	118.59	118.59	118.53	118.60	118.83

TABLE 3 (continued)

1	2	3	4	5	6	7	8	9	10	11
C-7	125.78	125.83	125.85	126.01	125.80	125.81	125.82	125.78	125.98	125.92
C-8	109.34	109.15	109.12	108.80	109.36	109.14	109.11	109.34	108.60	108.60
C-8a	141.51	141.05	139.96	140.43	140.52	141.03	139.94	140.49	140.45	140.42
NCH_3		28.95				28.94				
NCH_2CH_3			36.93	37.63			36.92		37.62	37.60
			13.58	13.81			13.58		13.77	13.80
$NCH_2CH_2 CH_3$	43.67, 21.77, 11.26				43.68 21.78, 11.26			43.68 21.78, 11.26		
C-2', CO (C-4") C-b'	171.26 or 174.37	170.91 or 173.18	170.93 or 173.20	171.49 or 173.12	170.93 or 173.20	171.40 or 171.57	171.44 or 171.60	171.43 or 171.58	171.85 or 172.49	171.79 or 174.32 or 169.42
C-3'		34.81	34.80	35.37	34.80	35.48	35.49	35.48	35.29	34.18
C-4'		35.07	35.10	36.13	35.11	34.26	34.33	34.33	36.49	35.10
C-5'		50.81	50.84	51.79	50.83	51.73	51.77	51.76	52.25	51.79
OCH_3		52.06	52.62	52.08	52.08					
a									152.94	146.93
a'									14.36 or 14.44	14.17
b									111.83	44.57
c									144.36	60.21
c'									14.36 or 14.44	15.65

* The ^{13}C NMR spectra were obtained in deuterochloroform.

compounds **7-9** had a screening action (about 0.8 ppm) on the chemical shift of the C(4') atom compared with the investigated compounds **4-6**, **16**, and **18**. On account of the structural and steric characteristics of the synthesized compounds the assignment of the signals of the CO groups in the spectra is problematical. An unambiguous assignment of the signals requires further investigation of the synthesized compounds. The presence of signals for carbon atoms at 152.94 (a), 144 (c), and 111.83 (b) ppm indicated the formation of pyrazole ring [15-17] in compound **16**. The resonance signals of the carbon atoms for compounds **5**, **16**, and **18** in solutions in deuterochloroform were observed in the downfield region (with the exception of the signals of the C(1), C(3), and C(8) atoms) compared with the corresponding signals of compounds **4-9** in DMSO-d_6 solutions.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were obtained on Jeol FX 100 (100 MHz), Bruker AC 250 (250 MHz), and Bruker DRX 500 (500 MHz) spectrometers with TMS as internal standard. The IR spectra were recorded on a Perkin-Elmer BX FT-IR instrument in tablets with potassium bromide. The reactions and the purity of the obtained compounds were monitored by TLC on Silufol UV-254 plates with development in UV light or with iodine. For column chromatography we used silica gel L 40/100 (Chemapol).

The physicochemical and spectral characteristics of the synthesized compounds are given in Tables 1-3.

4-Methoxycarbonyl-1-(9-methyl-9H-carbazol-3-yl)-2-pyrrolidinone (4). Mixture of 4-carboxy-1-(9-methyl-9H-carbazol-3-yl)-2-pyrrolidinone (**1**) (7.7 g, 25 mmol), methanol (80 ml), and concentrated sulfuric acid (2.5 ml) was boiled for 6 h. The liquid fractions were distilled under vacuum on a rotary evaporator. The residue was mixed with 5% sodium carbonate solution (150 ml) and extracted with diethyl ether (3×100 ml). The extract was dried with anhydrous sodium carbonate, the solvent was distilled under vacuum on a rotary evaporator, and compound **4** was isolated by chromatography of the residue in the 1:1.5 acetone–hexane system.

1-(9-Ethyl-9H-carbazol-3-yl)-4-methoxycarbonyl-2-pyrrolidinone (5). The compound was obtained from 4-carboxy-2-pyrrolidinone (**2**) (8.0 g, 25 mmol) by analogy with compound **4**.

4-Methoxycarbonyl-1-(9-propyl-9H-carbazol-3-yl)-2-pyrrolidinone (6). The compound was obtained from 4-carboxy-2-pyrrolidinone (**3**) (8.4 g, 25 mmol) by analogy with compound **4**.

1-(9-Methyl-9H-carbazol-3-yl)-5-oxo-3-pyrrolidinecarbohydrazide (7). Mixture of methyl ester **4** (6.44 g, 20 mmol), hydrazine hydrate (2.9 g, 60 mmol), and ethanol (20 ml) was boiled for 30 min. On cooling the separated crystals of compound **7** were filtered off and washed with ethanol and with ether.

1-(9-Ethyl-9H-carbazol-3-yl)-5-oxo-3-pyrrolidinecarbohydrazide (9). The compound was obtained from methyl ester **6** (7.0 g, 20 mmol) by analogy with compound **7**.

N-[(4-Dimethylaminophenyl)methylidene]-5-oxo-1-(9-ethyl-9H-carbazol-3-yl)-3-pyrrolidinecarbohydrazide (10). Mixture of hydrazide **8** (1.0 g, 3.0 mmol), dimethylaminobenzaldehyde (0.53 g, 3.0 mmol) and 1,4-dioxane (10 ml) was boiled for 2 h, and the solvent was distilled under vacuum on a rotary evaporator. The residue was treated with diethyl ether (20 ml) and filtered. Compound **10** was isolated by chromatography in the 2:1:1 acetone–hexane–chloroform system.

N-[(9-Ethyl-9H-carbazol-3-yl)methylidene]-5-oxo-1-(9-ethyl-9H-carbazol-3-yl)-3-pyrrolidinecarbohydrazide (11). This compound was obtained from hydrazide **8** (1.0 g, 3.0 mmol), 9-ethyl-3-formylcarbazole (0.67 g, 3.0 mmol) by analogy with compound **10**. The product was purified by crystallization from 1:1 mixture of dioxane and 2-propanol.

N-[(4-Dimethylaminophenyl)methylidene]-N'-ethyl-5-oxo-1-(9-ethyl-9H-carbazol-3-yl)-3-pyrrolidinecarbohydrazide (12). Mixture of compound **10** (1.0 g, 2.0 mmol), powdered potassium hydroxide (0.20 g, 4.0 mmol), potassium carbonate (1.0 g), and iodoethane (30 ml) was boiled for 1 h, acetone (30 ml) was added, and the mixture was filtered. The filtrate was evaporated under vacuum on a rotary evaporator, and compound **12** was isolated by chromatography of the residue in the 1:1 acetone–hexane system.

N-[(9-Ethyl-9H-carbazol-3-yl)methylidene]-N'-ethyl-5-oxo-1-(9-ethyl-9H-carbazol-3-yl)-3-pyrrolidine-carbohydrazide (13). This compound was obtained from compound **11** (1.08 g, 2.0 mmol) by analogy with compound **12**.

4-(5-Hydroxy-3,5-dimethyl-4,5-dihydropyrazolo-1-carbonyl)-1-(9-ethyl-9H-carbazol-3-yl)-2-pyrrolidinone (14). Mixture of hydrazide **8** (1.0 g, 3.0 mmol), methanol (15 ml), and acetylacetone (0.6 ml, 6.0 mmol) was stirred at 20°C for 7 h. The liquid fractions were removed under vacuum on a rotary evaporator (at temperature no higher than 40°C). The substance **14** was isolated by chromatography of the residue in the 1:1.5 acetone–hexane system.

4-(5-Hydroxy-3,5-dimethyl-4,5-dihydropyrazolo-1-carbonyl)-1-(9-propyl-9H-carbazol-3-yl)-2-pyrrolidinone (15). This compound was obtained from hydrazide **9** (1.0 g, 3.0 mmol) and acetylacetone (0.6 ml, 6.0 mmol) by analogy with compound **14**.

4-(3,5-Dimethylpyrazolo-1-carbonyl)-1-(9-ethyl-9H-carbazol-3-yl)-2-pyrrolidinone (16). Mixture of hydrazide **8** (1.0 g, 3.0 mmol), methanol (30 ml), acetylacetone (0.6 ml, 6.0 mmol), and 2 M hydrochloric acid (0.3 ml) was boiled for 4 h and cooled. The crystals of compound **16** that separated were filtered off and washed with methanol and with ether.

4-(3,5-Dimethylpyrazolo-1-carbonyl)-1-(9-propyl-9H-carbazol-3-yl)-2-pyrrolidinone (17). This compound was obtained from hydrazide **9** (1.0 g, 3.0 mmol) and acetylacetone (0.6 ml, 6.0 mmol) by analogy with compound **16**.

Ethyl 3-(2-{[5-Oxo-1-(9-ethyl-9H-carbazol-3-yl)-3-pyrrolidinyl]carbonyl}hydrazono)butanoate (18). Mixture of hydrazide **8** (2.0 g, 6.0 mmol), acetoacetic ester (1.56 g, 12 mmol), 2M hydrochloric acid (0.3 ml), and ethanol (10 ml) was heated at 60°C for 1 h 30 min. The solvent was evaporated under vacuum on a rotary evaporator. Compound **18** was isolated by chromatography of the residue in the 5:1 acetone–hexane system.

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