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Synthesis and structure of new 1,3-disubstituted 5-oxopyrrolidine derivatives

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A novel series of 1,3-disubstituted pyrrolidinone derivatives with aromatic, hydrazone, azole, diazole and triazole moieties has been prepared from 3-carbohydrazides of 1-phenyl-5-oxopyrrolidine and 1-(4-bromophenyl)-5-oxopyrrolidine. The structure of all the study compounds has been confirmed on the basis of NMR, IR, mass spectra, and elemental analyses data. In some cases, molecular modeling was used for determining the spatial structure.

Key words: 5-oxo-1-phenylpyrrolidine-3-carbohydrazides, cyclization, azoles, isomerism, NMR spectroscopy

INTRODUCTION

Five-membered heterocyclic compounds containing one, two or three nitrogen atoms in the ring are of considerable pharmaceutical and material interest. The pyrrole ring system is involved in coloured products (chlorophyll, hemoglobin, indigo) in nature; they are widely used as intermediates in the synthesis of pharmaceuticals [1–3], agrochemicals [4], dyes [5], as catalysts for polymerization process [6], corrosion inhibitors [7], and in other fields of chemistry and industry. A large number of 1,3,4-oxadiazoles has been described in numerous publications because of their application as pharmaceutical preparations [8], crop protectors [9]. 1,3,4-Oxadiazole derivatives also lie in the fields of photosensitizers [10] and liquid crystals [11]. 1,2,4-Triazole and its derivatives are known as pharmaceuticals [12–15] and agrochemicals [16] which treat and control various diseases. 1,2,4-Triazole is used as an intermediate for phytosanitary and pesticide products, photoconductors, and copying systems.

Taking into account a wide variety of application of heterocyclic compounds and their intermediates, the synthesis and structure investigation are of considerable interest. Many works are devoted to the study of compounds that include amide, azomethine groups [17–31], and heterocycles containing N, O, and S atoms [32–48]. Continuing our previous works [27–31], we report in this paper the synthesis and structure characterization of some new 1,3-disubstituted 5-oxopyrrolidine derivatives (Scheme).

RESULTS AND DISCUSSION

The corresponding hydrazones **2–6** were synthesized in good yields by reacting acid hydrazides **1a, b** with aromatic aldehydes in 2-propanol at reflux. The structure of **2–6** has been established mainly on the basis of ^{1}H and ^{13}C NMR spectra. NMR spectra have the characteristic pattern of monosubsti-

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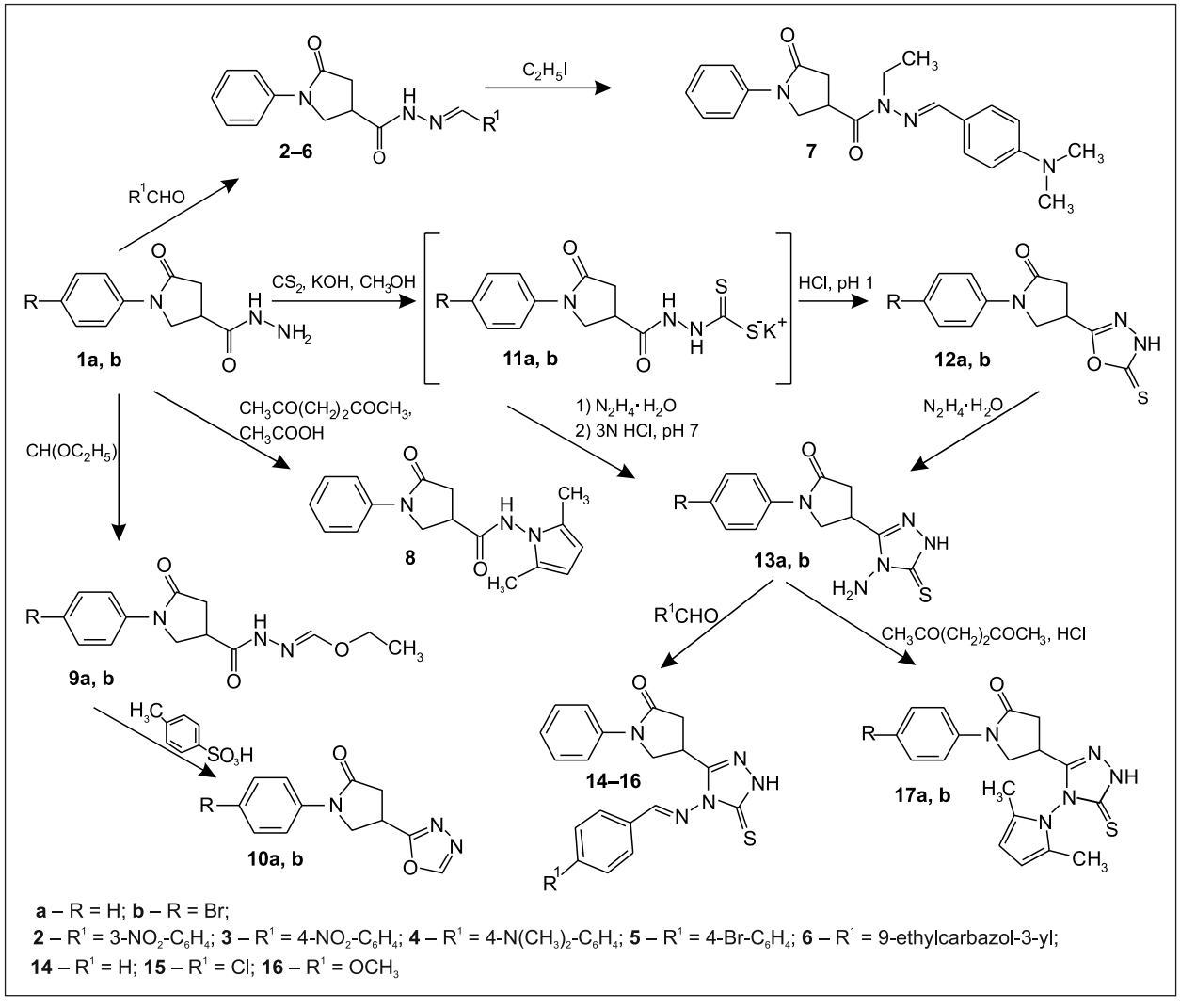

Scheme. Synthesis of new 1,3-disubstituted 5-oxopyrrolidine derivatives

tuted benzene and multiplets of the pyrrolidinone moiety common to all **a**-type study compounds. Compounds **2–6**, containing amide and azomethine groups, can exist theoretically as an inseparable mixture of four izomers. The amide group determines the splitting of resonances in ^{1}H and ^{13}C NMR spectra due to the restricted rotation around the amide bond (*Z/E*). The lone pair of the nitrogen atom in the azomethine group affects the neighbouring atoms and causes formation of geometrical isomers (*cis/trans*) [27–31]. The ^{13}C NMR spectra of **2–6** exhibited the double set of resonances of CO, N=CH, pyrrolidinone ring carbons and even some carbons (C-1, 2, 6) of the benzene ring. The decay of the differences of the corresponding averaged chemical shifts ~4.80 ppm (CO), ~3.30 ppm (N=CH) and ~2.00 ppm (C-3'), ~0.70 ppm (C-4'), ~0.44 ppm (C-2'), and ~0.20 ppm (C-5') demonstrates the presence of only one centre of isomerism (*Z/E*). The data presented above let us to conclude that geometrical isomers (*cis/trans*) of the azomethine group are not observed. The substituents attached to the benzene ring were found to influence the chemical shift values of CH in the azomethine group.

Alkylation of 1-aryl-3-arylidenehydrazinocarbonyl-5-oxopyrrolidine **4** with iodoethane was investigated. The reaction was carried out in a large excess of iodoethane in the presence of potassium hydroxide and potassium carbonate, and compound **7** was isolated in 83% yield. The single set of resonances in NMR spectra of **7** clearly proved the NH group alkylation.

The absorption band characteristic of the NH group is absent in the IR spectra of **7**, contrary to the initial compound **4**. The spectral data of all study compounds are given in the Experimental section.

Carbohydrazide **1a** easily reacted with diketone – 2,5-hexanedione in the presence of acetic acid, and 4-[4-(2,5-dimethyl-1*H*-pyrrol-1-yl)-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-1-phenylpyrrolidin-2-one (**8**) was isolated from the reaction mixture. The double-intensity resonances at 10.71 ppm (CH_3), 102.87 ppm (CH) in ^{13}C NMR spectra and 2.02 ppm (CH_3), 5.67 ppm (CH) in ^{1}H NMR indicated the formation of a pyrrole ring in compound **8**. It was shown [29, 31] that, in spite of the presence of the amide group, no isomers formation was observed in DMSO-d_6 solution.

Monosubstituted derivatives of oxadiazole can be obtained directly from acid hydrazides and triethyl orthoformate. Refluxing hydrazides **1a, b** in the excess of triethyl orthoformate, in the presence of *p*-toluenesulfonic acid, afforded 2-substituted oxadiazoles **10a, b**. Shortening of the reaction time in the absence of *p*-toluenesulfonic acid led to separation of hydrazone-type intermediates **9a, b** containing amide, azomethine and ethereal fragments. Their presence determined the specific structural features of the compounds.

The NMR spectra of compounds **9a, b** exhibit four sets of resonances. Differently from **2–6**, these compounds **(9a, b)** really exist in four different spatial states (*Z*/*cis*, *Z*/*trans*, *E*/*cis*, *E*/*trans*). A comparison of NMR spectra in DMSO-d_6 and $CDCl_3$ revealed different spatial structures in these solvents. The intensity of resonances depended on the solvent: in DMSO-d_6 the intensity of NH and CH protons of compound **9b** was distributed as 0.18 : 0.41 : 0.14 : 0.27, while in case of $CDCl_3$, as 0.05 : 0.15 : 0.74 : 0.06. This allowed us to conclude that the isomerism of the azomethine group is possible at a temperature of spectrum registration.

The existence of partially double bonds in CONHN-$CHOCH_2CH_3$ fragment of the optimized model of molecule **9b** is shown in Figure. The formation of such bonds in the molecules of these compounds implies rotation around the NCH bond in the azomethine group.

The singlet at 9.24 ppm in ^{1}H NMR spectrum, two resonances at 154.91 ppm, 166.45 ppm in ^{13}C NMR spectrum of compound **10** are in agreement with the structure of the 1,3,4-oxadiazole ring and can be attributed to CH and O–C=N fragments, respectively.

The present work was aimed at synthesizing triazole derivatives with a functional amino group in the five-membered heterocyclic ring. For this purpose, carbohydrazides **1a, b** were converted to the corresponding potassium dithiocarbazates **11a, b** by heating with carbon disulfide in methanol at reflux in the presence of potassium hydroxide. Then, potassium dithiocarbazates **11a, b** were heated with hydrazine hydrate, the reaction mixture was acidified with diluted hydrochloric acid, and the corresponding 4-(4-amino-4,5-dihydro-5-thioxo-1*H*-1,2,4-triazol-3-yl)-1-arylpyrrolidin-2-ones **13a, b** were obtained.

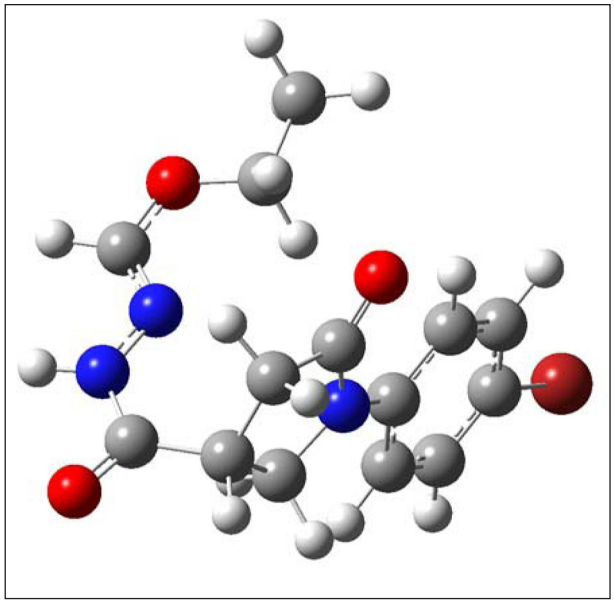

Figure. Optimized spatial structure of compound 9b, obtained using Gaussian G3W package

The other way of synthesis of amino triazoles **13a, b** is heating of the corresponding 1,3,4-oxadiazoles **12a, b** with hydrazine hydrate. Oxadiazoles **12a, b** were synthesized from the intermediates – potassium dithiocarbazates **11a, b** – by acidifying the reaction mixture with diluted hydrochloric acid to pH 1. The resonances at about 163.80 ppm, 177.98 ppm in the ^{13}C NMR spectra and a broadened singlet at 14.45 ppm in the ^{1}H NMR spectra assigned to the C=N, C=S, NH groups, respectively, indicated the formation of the proposed 5-membered heterocycle ring in compounds **12a, b**.

In the IR spectrum of compound **12b**, the absorption band observed at 3 051 cm^{-1} is characteristic of the NH group. Absorption bands at 1 653 cm^{-1}, 1 497 cm^{-1} and 1 318 cm^{-1} were ascribed to the C=O group of the pyrrolidinone ring, the C=N group of the oxadiazole ring, and the C=S group, respectively.

The appearance of new, more shielded in comparison with **12a, b**, (C=N, C=S) carbon nuclei resonances at about 152.50 ppm and 167.25 ppm, respectively, in ^{13}C NMR spectra revealed the composition of the triazole derivatives **13a, b**. A sharp singlet at about 5.50 ppm (NH_2) integrated for two protons, and a broadened singlet at about 13.45 ppm integrated for one proton (NH) in ^{1}H NMR spectra confirm formation of the above-mentioned heterocycle.

Condensation reactions of aminotriazole **13a** with aromatic aldehydes were carried out, and the corresponding Schiff bases **14–16** were obtained. ^{13}C NMR spectra exhibited two resonances at about 151.40 ppm and 162.00 ppm (for C=N and C=S, respectively) characteristic of the triazole ring, one more resonance at about 162.00 ppm belonging to N=CH group and six additional signals resonating in the aromatic region confirmed the suggested structures of compounds **14–16**. The proposed structure of **14–16** was confirmed by a singlet of the NH group at about 13.90 ppm and a newly observed singlet at about 10.00 ppm of the N=CH fragment in ^{1}H NMR spectra, while the signal originating from NH_2 disappeared.

During the condensation reactions of 4-amino-1,2,4-triazoles **13a, b** with 2,5-hexanedione, performed in the refluxing 2-propanol in the presence of a catalytic amount of hydrochloric acid, *N*-substituted pyrrole derivatives **17a, b** were synthesized. The resonances at about 151.40 ppm, 167.00 ppm, characteristic of triazole ring carbons, and the double intensity signals observed at 10.92 ppm of CH_3, CH signals at about 127.40 ppm in the ^{13}C NMR spectra, and the respective singlets at 1.97 (CH_3), 5.92 (CH), 14.26 (NH)

in ^{1}H NMR spectra validated the structure of **17a, b** compounds.

To conclude, 5-oxo-1-phenylpyrrolidine-3-carbohydrazides are excellent intermediates for the synthesis of potentially biologically active 1,3-disubstituted pyrrolidinone derivatives with aromatic, hydrazone, azole, diazole and triazole moieties.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Inova (300 MHz, 75 MHz) spectrometer operating in the Fourier transform mode, using DMSO-d_6 and $CDCl_3$ as solvents and TMS as an internal reference (chemical shifts in δ, ppm). IR spectra (ν, cm^{-1}) were recorded on a Perkin Elmer Spectrum BX FT–IR spectrometer using KBr tablets. Mass spectra were obtained with a Waters ZQ 2000 spectrometer using the atmospheric pressure chemical ionization (APCI) mode and operating at 25 V. Elemental analyses were performed with a CE-440 elemental analyzer. Melting points were determined on an automatic APA1 melting point apparatus and are uncorrected. TLC was performed with Merck, Silica gel 60 F_{254} (Kieselgel 60 F_{254}) silica gel plates.

General procedure for the synthesis of hydrazones 2–6. A mixture of hydrazide **1a** (1.0 g, 4.6 mmol) and 5 mmol of the corresponding aromatic aldehyde in 25 ml of 2-propanol was heated under reflux for 6 h. The reaction mixture was cooled to room temperature, the precipitate was filtered off, washed with 2-propanol and crystallyzed from the appropriate solvent.

N'-[(3-Nitrophenyl)methylidene]-5-oxo-1-phenylpyrrolidine-3-carbohydrazide (2)

Yield 1.3 g (81%), m. p. 208–209 °C (2-propanol). IR (ν, cm^{-1}): 3260 (NH), 1 700, 1 665 (C=O), 1 531 (C=N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.70–2.92 (m, 2H, CH_2CO), 3.28–3.44 (m, (0.4)1H, CH), 3.96–4.20 (m, 2H, CH_2N + (0.6) 1H, CH), 7.11–8.53 (m, 9H, H_{ar}), 8.16, 8.34 (2 s (0.6 : 0.4) 1H, N=CH), 11.82, 11.91 (2 s, (0.6:0.4) 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 32.78, 34.85 (Z/E, C-3'), 35.00, 35.65 (Z/E, C-4'), 49.97, 50.41 (Z/E, C-2'), 119.40, 119.45 (Z/E, C-2, 6), 121.13, 121.25 (Z/E, C-2''), 124.06, 124.30 (Z/E, C-4''), 124.12 (C-4), 128.68 (C-3, 5), 130.39 (C-5''), 132.81, 133.20 (Z/E, C-6''), 135.95, 136.03 (Z/E, C-1''), 139.12, 139.19 (Z/E, C-1), 141.49, 144.62 (Z/E, CH=N), 148.24 (C-3''), 169.06 (Z, CONH), 171.78, 171.98 (Z/E, C-5'), 173.86 (E, CONH). Anal. calcd. for $C_{18}H_{16}N_4O_4$, %: C, 61.36; H, 4.58; N, 15.90. Found, %: C, 61.62; H, 4.29; N, 15.85.

N'-[(4-Nitrophenyl)methylidene]-5-oxo-1-phenylpyrrolidine-3-carbohydrazide (3)

Yield 1.26 g (78%), m. p. 220–221 °C (2-propanol). IR (ν, cm^{-1}): 3 124 (NH), 1 683, 1 656 (C = O), 1 585 (C = N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.71–2.92 (m, 2H, CH_2CO), 3.29–3.44 (m, 0.4 (1H), CH), 3.97–4.20 (m, 2H, CH_2N + 0.6(1H), CH), 7.11–8.32 (m, 9H, H_{ar} + 1H, CH), 11.88, 11.94 (2 s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 32.86 (Z, C-3'), 34.93 (C-4'), 36.62 (E, C-3'), 45.92, 50.36 (Z/E, C-2'), 119.39, 119.47 (Z/E, C-2, 6), 124.01 (C-4 + C-3'', 5''), 127.84, 127.99 (Z/E, C-2'', C-6''), 128.68, 128.86 (Z/E, C-3'', 5''), 139.12 (C-1), 140.39, 140.45 (Z/E, C-1''), 141.34, 144.57 (Z/E, CH=N), 147.68, 147.85 (C-3''), 169.13 (Z, CONH), 171.75, 171.93 (Z/E, C-5'), 173.95 (E, CONH). Anal. calcd. for $C_{18}H_{16}N_4O_4$, %: C, 61.36; H, 4.58; N, 15.90. Found, %: C, 61.15; H, 4.47; N, 16.02.

N'-{[4-(Dimethylamino)phenyl]methylidene}-5-oxo-1-phenylpyrrolidine-3-carbohydrazide (4)

Yield 1.1 g (69%), m. p. 228–229 °C (2-propanol). IR (ν, cm^{-1}): 3 222 (NH), 1 702, 1 675 (C=O), 1 601 (C=N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.74–2.82 (m, 2H, CH_2CO), 2.94, 2.95 (2 s, 3H, $N(CH_3)_2$), 3.26–3.43 (m, (0.4)1H, CH), 3.92–4.16 (m, 2H, CH_2N + (0.6)1H, CH), 6.70–7.69 (m, 9H, H_{ar}), 7.91, 8.07 (2 s, (0.6:0.4)1H, CH=N), 11.30, 11.35 (2s, (0.6 : 0.4)1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 32.86, 34.78 (Z/E, C-3'), 34.97, 35.77 (C-4'), 50.13, 50.60 (Z/E, C-2'), 111.79 (C-3'',5''), 119.36, 119.43 (Z/E, C-2, 6), 121.33, 121.49 (C-1''), 123.99 (C-4), 128.11, 128.40 (Z/E, C-2'',6''), 128.67 (C-3, 5), 139.17, 139.24 (C-1), 141.43, 147.82 (Z/E, CH=N), 151.34, 151.51 (C-4''), 167.99 (Z, CONH), 171.93, 172.13 (Z/E, C-5'), 172.88 (E, CONH). Anal. calcd. for $C_{20}H_{22}N_4O_2$, %: C, 68.55; H, 6.33; N, 15.99. Found, %: C, 68.29; H, 6.53; N, 16.08.

N'-[(4-Bromophenyl)methylidene]-5-oxo-1-phenylpyrrolidine-3-carbohydrazide (5)

Yield 1.57 g (89%), m. p. 223–224 °C (ethanol). IR (ν, cm^{-1}): 3 263 (NH), 1 668, 1 655 (C=O), 1 600 (C=N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.69–2.90 (m, 2H, CH_2CO), 2.28–3.43 (m, (0.4)1H, CH), 3.95–4.17 (m, 2H, CH_2N + (0.6)1H, CH), 7.11–7.68 (m, 9H, H_{ar}), 8.01, 8.20 (2 s, (0.6:0.4)1H, CH=N), 11.65, 11.72 (2 s, (0.6:0.4)1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 32.82, 34.83 (Z/E, C-3'), 34.95, 35.66 (C-4'), 49.99, 50.43 (Z/E, C-2'), 119.38, 119.45 (Z/E, C-2, 6), 123.08, 123.34 (C-4''), 124.03 (C-4), 128.67, 128.76 (Z/E, C-3,5), 128.92 (C-2'', 6''), 131.80 (C-3'', 5''), 133.40 (C-1''), 139.13, 139.19 (C-1), 142.48, 145.78 (Z/E, CH=N), 168.75 (Z, CONH), 171.81, 171.99 (Z/E, C-5'), 173.60 (E, CONH). Anal. calcd. for $C_{18}H_{16}BrN_3O_2$, %: C, 55.97; H, 4.18; N, 20.69. Found, %: C, 55.71; H, 4.31; N, 20.51.

N'-[(9-Ethyl-9H-carbazol-3-yl)methylidene]-5-oxo-1-phenylpyrrolidine-3-carbohydrazide (6)

Yield 1.8 g (87%), m. p. 201–202 °C (ethanol). IR (ν, cm^{-1}): 3 196 (NH), 1 701, 1 668 (C=O) 1 597 (C=N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 1.31, 1.32 (2 t, J = 7.1 Hz, $CH_2\underline{CH_3}$), 2.72–2.96 (m, 2H, CH_2CO), 3.30–3.43 (m, (0.4)1H, CH), 3.98–4.25 (m, 2H, CH_2N + (0.6)1H, CH), 4.45 (k, J = 7.1 Hz, $\underline{CH_2}CH_3$), 7.14–8.46 (m, 5H, H_{ar} + 7H, $H_{carbazol}$ + 1H, N=CH), 11.53, 11.59 (2 s, (0.6 : 0.4)1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6,

δ, ppm): 13.73 ($NCH_2\underline{CH_3}$), 32.84, 34.85 (Z/E, C-3'), 35.08, 35.80 (Z/E, C-4'), 37.12 (NCH_2CH_3), 50.17, 50.62 (Z/E, C-2'), 109.60, 109.44 (C-1'', 8''), 119.27 (C-6''), 119.39, 119.46 (Z/E, C-2, 6), 120.23, 120.28, 120.62, 120.70 (C-4'', C-5''), 122.10 (5a''), 122.32 (4a''), 124.04, 124.54 (Z/E, C-4), 125.05, 125.13 (C-2''), 126.19 (C-3''), 128.69 (C-3,5), 139.18, 139.26 (Z/E, C-1), 139.95 (C-8a), 140.46, 140.63 (C-1a''), 144.94, 148.26 (Z/E, CH=N), 168.34 (Z, CONH), 171.94, 172.18 (Z/E, C-5'), 173.27 (E, CONH). Anal. calcd. for $C_{26}H_{24}N_4O_2$, %: C, 73.57; H, 5.70; N, 13.20. Found, %: C, 73.62; H, 5.81; N, 13.10.

N'-{[4-(Dimethylamino)phenyl]methylidene}-N-ethyl-5-oxo-1-phenylpyrrolidine-3-carbohydrazide (7)

A mixture of hydrazone **4a** (3.54 g, 10 mmol), powdered KOH (50 mmol), K_2CO_3 (25 mmol) and iodoethane (30 ml) was heated at 50 °C for 4 h. After keeping at room temperature for 24 h, the mixture was diluted with acetone (50 ml), filtered, the filtrate was evaporated under reduced pressure, and the residue was diluted with water (50 ml). The precipitate was filtered off, washed with water and dried. Yield 3.4 g (83%), m. p. 175–176 °C (ethanol). IR (ν, cm^{-1}): 1 707, 1 658 (C=O), 1 599 (C=N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 1.08 (t, 3H, *J* = 7.0 Hz, $CH_2\underline{CH_3}$), 2.80, 2.83 (2 s, 2H, CH_2CO), 3.92–4.30 (m, 1H, CH + 2H, CH_2N, 2H, $\underline{CH_2}CH_3$), 6.73–7.67 (m, 9H, H_{ar}), 7.96 (1 s, 1H, CH=N). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 11.14 (CH_2CH_3), 33.48 ($\underline{CH_2}CH_3$), 34.88 (C-3'), 35.44 (C-4'), 39.77 ($N(CH_3)_2$), 50.55 (C-2'), 111.79 (C-3'', 5''), 119.39 (C-2,6), 122.31 (C-1''), 123.95 (C-4), 128.31, 128.65 (C-3,5; C-2'', 6''), 139.24 (C-1), 141.03 (CH-N), 151,25 (C-4''), 172.01, 172.13 (C-5'', $CONCH_2CH_3$). Anal. calcd. for $C_{22}H_{26}N_4O_2$, %: C, 69.82; H, 6.92; N, 14.80. Found, %: C, 69.71; H, 6.78; N, 14.66.

N-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-5-oxo-1-phenylpyrrolidine-3-carboxamide (8)

A mixture of 5-oxo-1-phenylpyrrolidine-3-carbohydrazide **1a** (1.1 g, 5 mmol), 2,5-hexanedione (0.86 g, 7.5 mmol), glacial acetic acid (1 ml) and ethanol (35 ml) was refluxed for 16 h, the solvent was separated under reduced pressure, the residue diluted with water (50 ml), and the solution was heated to gentle boiling. After cooling the reaction mixture, the precipitate was filtered off, washed with water and dried. Yield 1.12 g (75%), m. p. 135–136 °C (ethanol). IR (ν, cm^{-1}): 3 264 (NH), 1 687, 1 667 (C=O). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.02 (s, 6H, $2CH_3$), 2.77 (dd, 1H, *J* = 7.2 Hz, *J* = 17.1 Hz, CH_2CO), 2.91 (dd, 1H, *J* = 9.3 Hz, *J* = 17.1 Hz, CH_2CO), 3.50–3.60 (m, 1H, CH), 4.01 (dd, 1H, *J* = 5.7 Hz, *J* = 9.9 Hz, CH_2N), 4.15 (dd, 1H, *J* = 8.4 Hz, *J* = 9.9 Hz, CH_2N), 5.67 (s, 2H, 2CH), 7.11–7.77 (m, 5H, H_{ar}), 10.94 (s, (1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 10.71 (CH_3), 33.75 (C-3'), 35.34 (C-4'), 50.03 (C-2'), 102.76 (C=CH), 120.24 (C-2, 6), 123.61 (C-1), 126.52 ($\underline{C}CH_3$), 128.21 (C-3, 5), 139.69 (C-1), 170.66, 172.01 (C-5', CONH). MS (*m/z*, %): $[M+H]^+$ 298 (100), ($[M+1+H]^+$ 299 (20). Anal. calcd. for $C_{17}H_{19}N_3O_2$, %: C, 68.67; H, 6.44; N, 14.13. Found, %: C, 68.82; H, 6.42; N, 14.07.

General procedure for the synthesis of ethyl [(5-oxo-1-phenylpyrrolidin-3-yl)carbonyl]hydrazonoformates 9a, b

A mixture of the corresponding 5-oxo-1-phenylpyrrolidine-3-carbohydrazide **1a, b** (5 mmol) and triethyl orthoformate (10 ml) was heated to boiling and then cooled to room temperature. The precipitate was filtered off, washed with ether and dried.

Ethyl [(5-oxo-1-phenylpyrrolidin-3-yl)carbonyl]hydrazonoformate (9a)

Yield 1.02 g (74%), m. p. 154–155 °C (2-propanol); IR (ν, cm^{-1}): 3 228 (NH), 1 694, 1 667 (C=O), 1 408 (C=N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 1.25, 1.26, 1.29 (3t; *J* = 7.1 Hz, 3H, CH_3), 2.58–2.79 (m, 2H, CH_2CO), 3.16–4.21 (m, 5H, $O\underline{CH_2}CH_3$ + CH + CH_2N), 6.86, 6.90 (2 s, (0.6)1H, CH), 7.10–7.16 (m, 1H, 4-H_{ar}), 7.33–7.40 (m, 2H, 3,5-H_{ar}), 7.62–7.66 (m, 2H, 2,6-H_{ar}), 7.94, 8.23 (2 s, (0,4)1H, CH), 10.04, 10.54, 10.76, 10.79 (4 s, (0.18 : 0.45 : 0.12 : 0.25)1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 14.09, 15.29, 15.50 ($OCH_2\underline{CH_3}$), 32.47, 32.57, 34.13, 34.68, 34.77, 34.97, 35.78, 35.87 (C-3', 4'), 49.91, 50.12, 50.64, 50.78 (C-2'), 62.46, 67.13 ($O\underline{CH_2}CH_3$), 119.34 (C-2, 6), 123.99 (C-4), 128.67 (C-3,5), 139.17 (C-1), 143.18, 145.41, 149.59, 155.40 (HC=N), 167.88, 168.47, 172.05, 172.57 (CONH + C-5'). ^{1}H NMR ($CDCl_3$, δ, ppm): 1.36, 1.37 (2t, *J* = 7.1 Hz, 3H, CH_3), 2.74–3.07 (m; 2H, CH_2CO), 3.90–4.25 (m, 5H, $O\underline{CH_2}CH_3$ + CH + CH_2N), 6.45, 6.68 (2 s, (0.95) 1H, CH), 7.11–7.17 (m, 1H, 4-H_{ar}), 7.31–7.38 (m, 2H, 3, 5-H_{ar}), 7.53–7.61 (m, 2H, 2, 6-H_{ar}), 7.79, 8.15 (2 s, (0.05)1H, CH), 8.78, 8.99, 9.52 (3 s, (0.79 : 0.17 : 0.04), 1H, NH). ^{13}C NMR ($CDCl_3$, δ, ppm): 15.30, 15.41 ($OCH_2\underline{CH_3}$), 33.34 (C3'), 35.26 (C-4'), 50.33, 50.91 (C-2'), 68.03, 68.32 ($O\underline{CH_2}CH_3$), 120.15 (C-2, 6), 124.66, 124.89 (C-4), 128.77 (C-3, 5), 138.92 (C-1), 141.83, 145.12, 152.26, 155.67 (HC=N), 167.60, 171.40, 172.20, 172.46 (CONH + C-5'). MS (*m/z*, %): $[M+H]^+$ 276 (20), $[M+Na]^+$ 298 (100). Anal. calcd. for $C_{14}H_{17}N_3O_3$, %: C, 61.08; H, 6.22; N, 15.26. Found, %: C, 61.18; H, 6.20; N, 15.28.

Ethyl {[1-(4-bromophenyl)-5-oxopyrrolidin-3-yl]carbonyl}-hydrazonoformate (9b)

Yield 1.36 g (78%), m. p. 180–181 °C (2-propanol). IR (ν, cm^{-1}): 3 220 (NH), 1 680, 1 664 (C=O), 1 494 (C=N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 1.25, 1.26, 1.29 (3 t, *J* = 7.1 Hz, 3H, CH_3), 2.58–2.79 (m, 2H, CH_2CO), 3.14–4.21 (m, 5H, $O\underline{CH_2}CH_3$ + CH + CH_2N), 6.86, 6.90 (2 s, (0.6)1H, CH), 7.52–7.57 (m, 2H, 2,6-H_{ar}), 7.62–7.66 (m, 2H, 3,5-H_{ar}), 7.94, 8.22 (2s, (0.4) 1H, CH), 10.06, 10.54, 10.76, 10.79 (4s, (0.18 : 0.41 : 0.14 : 0.27), 1H, NH). ^{1}H BMR, ($CDCl_3$, δ, ppm): 1.34, 1.38, 1.41 (3t, *J* = 7.1 Hz, 3H, CH_3), 2.74–3.04 (m, 2H, CH_2CO), 3.85–4.27 (m, 5H, $O\underline{CH_2}CH_3$ + CH + CH_2N), 6.46, 6.71 (2 s, (0.84) 1H, CH), 7.44–7.56 (m; 4H, H_{ar}), 7.61, 7.70 (2 s, (0.16) 1H, CH), 8.33, 8.36, 8.70, 8.76 (4s, (0.05 : 0.15 : 0.74 : 0.06) 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 14.07, 15.28, 15.50 ($OCH_2\underline{CH_3}$), 32.35, 33.68, 33.97, 34.52, 34.72, 34.91, 35.74, 35.82 (C-3',4'), 49.78, 49.98, 50.50, 50.65 (C-2'), 62.46,

62.52, 67.06, 67.12 (O$\underline{CH_2}CH_3$), 115.80 (C-4), 121.18 (C-2, 6), 131.45 (C-3, 5), 138.46 (C-1), 143.20, 145.43, 149.61, 155.41 (CH), 167.78, 168.38, 171.94, 172.20, 172.33, 172.44, 172.80 (CONH + C-5'). MS (*m/z*, %): 354 $[M+H]^+$ (45), $[M+1+H]^+$ 356 (45). Anal. calcd. for $C_{14}H_{16}BrN_3O_3$, %: C, 47.47; H, 4.55; N, 11.86. Found, %: C, 47.29; H, 4.56; N, 11.89.

General procedure for the synthesis of 1-aryl-4-(1,3,4-oxadiazol-2-yl)pyrrolidin-2-ones 10a, b

A mixture of 5-oxopyrrolidine-3-carbohydrazide **(1a, b)** (5 mmol), triethyl orthoformate (5.93 g, 40 mmol) and *p*-toluenesulfonic acid (0.19 g, 1 mmol) was refluxed for 20 h, cooled to room temperature, the precipitate filtered off, washed with hexane and dried.

4-(1,3,4-Oxadiazol-2-yl)-1-phenylpyrrolidin-2-one (10a)

Yield 1.02 g (89%), m. p. 135–136 °C (2-propanol). IR (ν, cm^{-1}): 1 693 (C=O), 1 595, 1 585 (C=N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.85–3.11 (m, 2H, CH_2CO), 4.08–4.34 (m, 1H, CH + 2H, CH_2N), 7.13–7.68 (m, 9H, H_{ar}), 9.24 (s, 1H, O-CH=N). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 27.64 (C-3'), 35.97 (C-4'), 50.60 (C-2'), 119.64 (C-2, 6), 124.30 (C-1), 128.71 (C-3, 5), 138.92 (C-1), 154.91 (N-C=N-O), 166.45 (OC=N-N), 171.49 (C-5'). Anal. calcd. for $C_{12}H_{11}N_3O_2$, %: C, 62.87; H, 4.84; N, 18.33. Found, %: C, 62.73; H, 4.96; N, 18.40.

1-(4-Bromophenyl)-4-(1,3,4-oxadiazol-2-y)pyrrolidin-2-one (10b)

Yield 0.6 g (39 %), m. p. 140–141 °C (2-propanol). IR (ν, cm^{-1}): 1 703 (C=O), 1 588, 1 576 (C=N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.85–3.11 (m, 2H, CH_2CO), 4.08–4.33 (m, 1H, CH + 2H, CH_2N), 7.55–7.66 (m, 9H, H_{ar}), 9.24 (s, 1H, O-CH=N). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 27.52 (C-3'), 35.91 (C-4'), 50.45 (C-2'), 116.16 (C-4), 121.45 (C-2, 6), 131.50 (C-3, 5), 138.23 (C-1), 154.91 (N-C=N-O), 166.33 (OC=N-N), 171.38 (C-5'). Anal. calcd. for $C_{12}H_{10}BrN_3O_2$, %: C, 46.78; H, 3.27; N, 13.64. Found, %: C 46.85; H 3.19; N 13.61.

General procedure for the synthesis of 1-phenyl-4-(5-thioxo-4,5-dihydro-1,3,4-oxadiazol-2-yl)pyrrolidin-2-ones 12a, b

A mixture of the corresponding 5-oxo-1-phenylpyrrolidine-3-carbohydrazide **1a, b** (5 mmol), potassium hydroxide (0.67 g, 12 mmol), carbon disulfide (0.57 g, 7,5 mmol) and anhydrous 2-propanol (30 ml) was refluxed for 6 h, cooled to room temperature, diluted with water (20 ml) and acidified with diluted hydrochloric acid (1 : 1) to pH 1. The precipitates of compounds **12a, b** were filtered off, washed with water and dried.

1-Phenyl-4-(5-thioxo-4,5-dihydro-1,3,4-oxadiazol-2-yl)-pyrrolidin-2-one (12a)

Yield 0.86 g (66%), m. p. 175–176 °C (2-propanol). IR (ν, cm^{-1}): 3 046 (NH), 1 659 (C=O), 1 499 (C=N), 1 316 (C=S). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.08 (s, (0,2)1H, SH), 2.80–3.03 (m, 2H, CH_2CO), 3.91–4.00 (m, 1H, CH), 4.06–4.25 (m, 2H, CH_2N), 7.15 (t, 1H, J = 7.4 Hz, 4-H_{ar}), 7.38 (t, J = 7.4 Hz, 3,5-H_{ar}), 7.64 (t, J = 7.4 Hz, 2,6-H_{ar}), 14.46 (br. s, (0.8)1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 27.93 (C-3'), 35.14 (C-4'), 49.85 (C-2'), 119.65 (C-2, 6), 124.33 (C-4), 128.72 (C-3, 5), 138.87 (C1), 163.90 (O-C=N), 170.94, 171.99 (C-5'), 177.98 (C=S). MS (*m/z*, %): $[M+H]^+$ 262 (100), $[M+1+H]^+$ 263 (20). Anal. calcd. for $C_{12}H_{11}N_3O_2S$, %: C, 60.65; H, 5.66; N, 15.72. Found, %: C, 60.68; H, 5.64; N, 15.67.

1-(4-Bromophenyl)-4-(5-thioxo-4,5-dihydro-1,3,4-oxadiazol-2-yl)pyrrolidin-2-one (12b)

Yield 0.91 g (53%), m. p. 247–248 °C (2-propanol). IR (ν, cm^{-1}): 3 051 (NH), 1 653 (C=O), 1 497 (C=N), 1 318 (C=S). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.81–3.04 (m, 2H, CH_2CO), 3.81–4.02 (m, 1H, CH), 4.02–4.24 (m, 2H, CH_2N), 7.53–7.66 (m, 4H, H_{ar}), 14.45 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 27.80 (C-3'), 35.08 (C-4'), 49.71 (C-2'), 116.18 (C-2, 6), 131.49 (C-3, 5), 138.18 (C1), 163.77 (O-C=N), 171.18, (C-5'), 177.98 (C=S). MS (*m/z*, %): $[M+H]^+$ 340 (95), $[M+1+H]^+$ 342 (100). Anal. calcd. for $C_{12}H_{10}BrN_3O_2S$, %: C, 42.37; H, 2.96; N, 12.35. Found, %: C, 42.52; H, 2.97; N, 12.39.

General procedure for the synthesis of 4-(4-amino-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl)-1-phenylpyrrolidin-2-ones (13a, b)

A mixture of the corresponding 5-oxo-1-phenylpyrrolidine-3-carbohydrazide **1a, b** (30 mmol), potassium hydroxide (4.04 g, 72 mmol), carbon disulfide (3.42 g, 45 mmol) and anhydrous 2-propanol (65 ml) was refluxed for 5 h, cooled to room temperature to 15 °C, and diethyl ether (45 ml) was poured into the reaction mixture. The precipitate was filtered off, washed with diethyl ether (3 × 50 ml) and dried. A mixture of the obtained dry solid, hydrazine hydrate (90 mmol) and water (10 ml) was refluxed for 3 h (until the orange colour of the mixture turned into green), then the mixture was cooled to room temperature, diluted with water (25 ml) and neutralized with 3N hydrochloric acid to pH 7. The precipitates of compounds **13a, b** were filtered off, washed with water and dried.

4-(4-Amino-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl)-1-phenylpyrrolidin-2-one (13a)

Yield 3.60 g (44%), m. p. 245–246 °C (ethanol). IR (ν, cm^{-1}): 3 272, 3 180, 3 119 (NH, NH_2), 1 678 (C=O), 1 494 (C=N), 1 313 (C=S). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.82–3.02 (m, 2H, CH_2CO), 3.83–3.92 (m, 1H, CH), 4.06–4.26 (m, 2H, CH_2N), 5.28, 5.57 (s, 2H, NH_2), 7.14 (t, 1H, J = 7.4 Hz, 4-H_{ar}), 7.37 (t, J = 7.4 Hz, 1.1 Hz, 3,5-H_{ar}), 7.63 (t, J = 7.4 Hz, J = 1.1 Hz, 2,6-H_{ar}), 13.62 (br. s, (1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 27.33 (C-3'), 35.31 (C-4'), 50.44 (C-2'), 119.55 (C-2, 6), 124.17 (C-4), 128.70 (C-3, 5), 139.08 (C-1),

152.61 (N-C=N-NH), 167.25 (N=CS-NH), 171.69 (C-5'). MS (*m/z*, %): $[M+H]^+$ 276 (100), $[M+1+H]^+$ 277 (20). Anal. calcd. for $C_{12}H_{13}N_5OS$, %: C, 52.35; H, 4.76; N, 25.44. Found, %: C, 52.54; H, 4.78; N, 25.36.

4-(4-Amino-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl)-1-(4-bromophenyl)pyrroli-din-2-one (13b)

Yield 2.58 g (24%), m. p. 232–233 °C (ethanol). IR (ν, cm^{-1}): 3 099, 3 043, 2 940 (NH, NH_2), 1 670 (C=O), 1 493 (C=N), 1 313 (C=S). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.82–3.03 (m, 2H, CH_2CO), 3.83–3.92 (m, 1H, CH), 4.05–4.24 (m, 2H, CH_2N), 5.56 (s, 2H, NH_2), 7.53–7.63 (m, 4H, H_{ar}), 13.31 (br. s, (1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 27.19 (C-3'), 35.28 (C-4'), 50.29 (C-2'), 116.01 (C-4), 121.32 (C-2, 6), 131.48 (C-3, 5), 138.38 (C-1), 152.49 (N-C=N-NH), 167.24 (N=CS-NH), 171.92 (C-5'). MS (*m/z*, %): $[M+H]^+$ 354 (100), $[M+1+H]^+$ 356 (40). Anal. calcd. for $C_{12}H_{12}BrN_5OS$, %: C, 40.69; H, 3.41; N, 19.77. Found, %: C, 40.59; H, 3.43; N, 19.70.

1-Phenyl-4-{4-[(phenylmethylidene)amino]-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl}-pyrrolidin-2-one (14)

A mixture of 4-(4-amino-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl)-1-phenylpyrrolidin-2-one **13a** (0.27 g, 1 mmol), benzaldehyde (0.21 g, 2 mmol), ethanol (8 ml) and hydrochloric acid (0.1 ml) was refluxed for 6 h, then cooled down. The precipitate of compound **14** was filtered off, washed with ethanol and dried. Yield 0.18 g (49%), m. p. 213–214 °C (a mixture of 1,4-dioxane and water). IR (ν, cm^{-1}): 3 099 (NH), 1 674 (C=O), 1 500 (C=N), 1 317 (C=S). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.86–3.01 (m, 2H, CH_2CO), 3.99–4.27 (m, 1H, CH + 2H, CH_2N), 7.40–7.90 (m, 9H, H_{ar}), 10.13 (s, 1H, CH = N), 13.92 (s, (1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 27.19 (C-3'), 35.35 (C-4'), 50.21 (C-2'), 119.53 (C-2, 6), 124.10 (C-4), 128.58 (C-3, 5), 128.60 (C-3",5"), 129.13 (C-2",6"), 132.10 (C-4"), 132.65 (C-1"), 138.95 (C-1), 151.36 (N-C=N-NH), 162.02, 162.73 (NHCS-N, N=CHPh), 171.73 (C-5'). Anal. calcd. for $C_{19}H_{17}N_5OS$, %: C, 62.79; H, 4.71; N, 19.27. Found, %: C, 62.56; H, 4.73; N, 19.21.

4-{4-[((4-Chlorophenyl)methylidene)amino]-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl}-1-phenylpyrrolidin-2-one (15)

A mixture of 4-(4-amino-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl)-1-phenyl-pyrrolidin-2-one **13a** (0.54 g, 2 mmol), 4-chlorobenzaldehyde (0.34 g, 2.4 mmol), ethanol (5 ml) and hydrochloric acid (0.1 ml) was refluxed for 2 h, then cooled to room temperature. The precipitate was filtered off, washed with ethanol and dried to give **15**. Yield 0.60 g (75%), m. p. 225–226 °C (a mixture of 1,4-dioxane and water). IR (ν, cm^{-1}): 3 211 (NH), 1 675 (C=O), 1 476, 1 411 (C=N), 1 266 (C=S). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.85–3.05 (m, 2H, CH_2CO), 3.99–4.27 (m, 1H, CH + 2H, CH_2N), 7.11–7.93 (m, 9H, H_{ar}), 10.13 (s, 1H, CH=N), 13.94 (s, (1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 27.29 (C-3'), 36.42 (C-4'), 50.27 (C-2'), 119.59 (C-2, 6), 124.17 (C-4), 128.66 (C-3, 5), 129.29 (C-3", 5"), 130.24 (C-2", 6"), 131.05 (C-1"), 137.26 (C-4"), 139.01 (C-1), 151.49 (N-C=N-NH), 161.07, 162.02 (NHCS-N, N=CHPh), 171.49 (C-5'). MS (*m/z*, %): $[M+H]^+$ 398 (50), $[M+1+H]^+$ 399 (20). Anal. calcd. for $C_{19}H_{16}ClN_5OS$, %: C, 57.35; H, 4.05; N, 17.60. Found, %: C, 57.18; H, 4.05; N, 17.65.

4-{4-[((4-Methoxyphenyl)methylidene)amino]-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl}-1-phenylpyrrolidin-2-one (16)

A mixture of 4-(4-amino-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl)-1-phenylpyrrolidin-2-one **13a** (0.54 g, 2 mmol), 4-methoxybenzaldehyde (0.54 g, 4 mmol), ethanol (5 ml) and hydrochloric acid (0.1 ml) was refluxed for 8.5 h and cooled to room temperature. The precipitate was filtered off, washed with ethanol and dried to give **16**. Yield 0.56 g (71%), m. p. 187–188 °C (a mixture of 1,4-dioxane and water). IR (ν, cm^{-1}): 3 101 (NH), 1 675 (C=O), 1 515, 1 501 (C=N), 1 261 (C=S). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.88 (dd, 1H, *J* = 6.6 Hz, *J* = 17.1 Hz, CH_2CO), 2.98 (dd, 1H, *J* = 9.0 Hz, *J* = 17.1 Hz, CH_2CO), 3.85 (s, 3H, OCH_3), 4.0–4.1 (m, 1H, CH), 4.10 (dd, 1H, *J* = 5.4 Hz, *J* = 9.9 Hz, CH_2N), 4.23 (dd, 1H, *J* = 8.4 Hz, *J* = 9.9 Hz, CH_2N), 7.11–7.96 (m, 9H, H_{ar}), 9.88 (s, 1H, CH=N), 13.90 (s, (1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 27.54 (C-3'), 35.62 (C-4'), 50.49 (C-2'), 55.74 (OCH_3), 114.83 (C-3", 5"), 119.80 (C-2, 6), 124.37 (C-1"), 124.68 (C-4), 128.66 (C-3, 5), 130.83 (C-2", 6"), 139.01 (C-1), 151.46 (N-C=N-NH), 162.19 (NHCS-N, N=CHPh), 163.44 (C-4"), 171.49 (C-5'). MS (*m/z*, %): $[M+H]^+$ 394 (100), $[M+1+H]^+$ 395 (20). Anal. calcd. for $C_{20}H_{19}N_5O_2S$, %: C, 61.05; H, 4.87; N, 17.80. Found, %: C, 61.24; H, 4.89; N, 17.74.

General procedure for the synthesis of 4-[4-(2,5-dimethyl-1*H*-pyrrol-1-yl)-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-1-phenylpyrrolidin-2-ones 17a, b

A mixture of the corresponding 4-(4-amino-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl)-1-phenylpyrrolidin-2-one **13a, b** (1.5 mmol), 2,5-hexanedione (0.26 g, 2.25 mmol), concentrated hydrochloric acid (0.3 ml) and 2-propanol (50 ml) was refluxed for 7 h, the solvent was evaporated under reduced pressure, and the residue was diluted with water (30 ml). The precipitate was filtered off, washed with water and dried.

4-[4-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-1-phenylpyrrolidin-2-one (17a)

Yield 0.6 g (87%), m. p. 204–205 °C (1,4-dioxane). IR (ν, cm^{-1}): 3 111 (NH), 1 671 (C=O), 1 500 (C=N), 1 321 (C=S). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 1.98 (s, 6H, CH_3), 2.47–2.83 (m, 2H, CH_2CO), 3.47–3.58 (m, 1H, CH), 3.85–4.11 (m, 2H, CH_2N), 5.92 (s, 2H, CH), 7.11–7.63 (m, 5H, H_{ar}), 14.26 (s, (1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 10.91, 10.97 ($C\underline{C}H_3$), 27.19 (C-3'), 35.35 (C-4'), 50.21

(C-2'), 105.76 (C=CH), 118.89 (C-2, 6), 123.61 (C-4), 126.76 (CCH$_3$), 128.47 (C-3, 5), 139.56 (C-1), 151.89 (N-C=N-NH), 167.68 (NHCS-N), 170.66 (C-5' MS (*m/z*, %): $[M+H]^+$ 354 (100), $[M+1+H]^+$ 355 (20). Anal. calcd. for $C_{18}H_{19}N_5OS$, %: C, 61.17; H, 5.42; N, 19.81. Found, %: C, 61.00; H, 5.39; N, 19.88.

1-(4-Bromophenyl)-4-[4-(2,5-dimethyl-1*H*-pyrrol-1-yl)-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]pyrrolidin-2-one (17b)

Yield 0.53 g (82%), m. p. 201–202 °C (1,4-dioxane). IR (ν, cm^{-1}): 3101, 2939 (NH), 1714 (C=O), 1494 (C=N), 1326 (C=S). ^{1}H NMR (300 MHz, DMSO-d$_6$, δ, ppm): 1.97 (s, 6H, CH$_3$), 2.47–2.84 (m, 2H, CH$_2$CO), 3.47–3.59 (m, 1H, CH), 3.87–4.11 (m, 2H, CH$_2$N), 5.92 (s, 2H, CH), 7.55 (s, 4H, H$_{ar}$), 14.26 (br. s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d$_6$, δ, ppm): 10.92, 10.98 (CCH$_3$), 27.34 (C-3'), 35.39 (C-4'), 49.71 (C-2'), 105.77 (CH=C), 116.21 (C-4), 121.44 (C-2, 6), 127.35, 127.49 (CCH$_3$), 131.52 (C-3, 5), 138.08 (C-1), 151.84 (N-C=N-NH), 167.67 (N-CS-NH), 170.97 (C-5'). MS (*m/z*, %): $[M+H]^+$ 432 (40), $[M+1+H]^+$ 433 (20), $[M+Na]^+$ 454 (70), [M+1+H+Na] 456 (60). Anal. calcd. for $C_{18}H_{18}BrN_5OS$, %: C, 50.01; H, 4.20; N, 16.20. Found, %: C, 49.84; H, 4.21; N, 16.16.

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NAUJŲ 1,3-DIPAKEISTŲ 5-OKSOPIROLIDINO DARINIŲ SINTEZĖ IR STRUKTŪRA

S a n t r a u k a

Darbe susintetinta daug naujų 1,3-dipakeistų pirolidinono darinių, turinčių aromatinį, hidrazono, pirolo, diazolo, triazolo fragmentus. Gautų junginių struktūros ypatybės išsamiai ištirtos ir aptartos pasitelkus ^{1}H ir ^{13}C BMR spektrinės analizės duomenis, molekulių modeliavimą.