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# Spiroheterocyclization of Pyrrolobenzoxazinetriones under the Action of Thiobenzamide. Synthesis of Spiro[thiazolo-5,2'-pyrroles]

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**Abstract**—3-Acylpyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-triones regioselectively react with thiobenzamide forming substituted spiro[thiazolo-5,2'-pyrroles], whose structure was confirmed by X-ray diffraction analysis.

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Compounds containing thiazole fragment are often present among practically important substances, for example, antibacterial drugs of penicillin series (benzylpenicillin) [1], hypoglycemic preparations of thiazolidine class (ciglitazone) [2], vitamin $B_1$ [3], bioluminescent compounds (D-luciferin) [4] (Scheme 1).

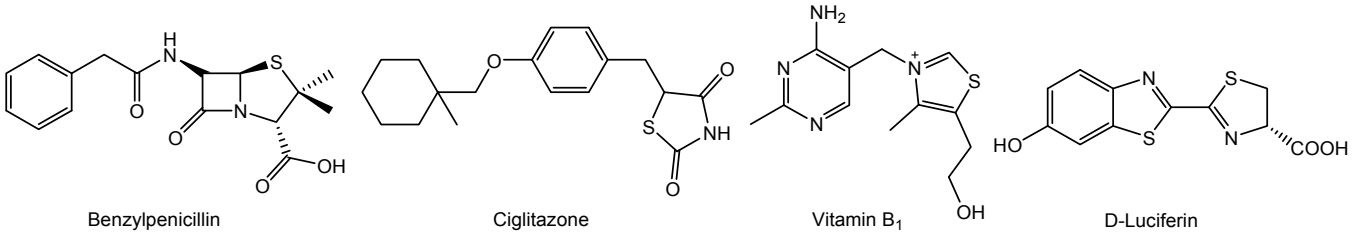
Spiroheterocyclizations of 5-acyl-substituted 1*H*-pyrrole-2,3-diones under the action of various 1,3-CH,NH- and 1,3-NH,NH-binucleophile reagents were studied for the synthesis of difficultly accessible heterocyclic systems of spiro[pyrrolo-3,2'-pyrrole] [5] and spiro[imidazolo-4,2'-pyrrole] [6] correspondingly. Spiroheterocyclizations of 5-acyl-subtituted 1*H*-pyrrole-2,3-diones under the action of 1,3-SH,NH-binucleophiles are poorly studied. The reaction of pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-triones with thiourea results in the formation of spiroheterocyclic system of spiro[imidazolo-4,2'-pyrrole] [7] instead of expected spiro[thiazolo-5,2'-pyrrole]. To synthesize previously inaccessible spiro[thiazolo-5,2'-pyrroles]-we studied the reaction of 3-acylpyrrolo[2,1-*c*][1,4]-benzoxazine-1,2,4-triones with thiobenzamide.

At boiling acylpyrrolobenzoxazinetriones **1a–1i** and thiobenzamide in anhydrous toluene during 20–40 min (till violet color of initial compounds **1a–1i** disappeared) we obtained the target spiro[thiazolo-5,2'-pyrroles] **2a–2i** [8], whose structure was proved by X-ray diffraction (XRD) analysis of compound **2b** (Scheme 2).

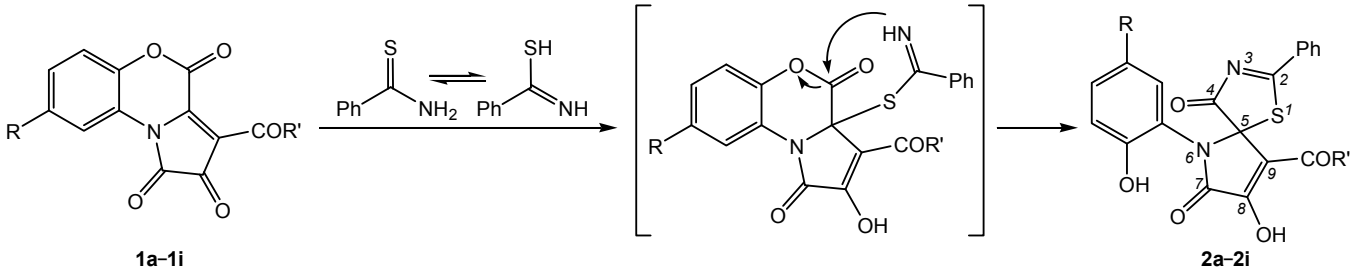
Compounds **2a–2i** are light-yellow high-melting crystalline substances melting with decomposition, easily dissolved in DMSO and DMF, soluble in aqueous-alcoholic mixtures, acetone, chloroform, 1,2-dichloroethane, 1,4-dioxane, ethyl acetate, sparingly soluble in aromatic hydrocarbons, tetrachloromethane, insoluble in alkanes and water, giving positive test (cherry coloring) on the presence of enol and phenol hydroxy groups with alcohol solution of iron(III) chloride.

In IR spectra of compounds **2a–2i** absorption bands of stretching vibrations of OH groups (3180–3516 $cm^{-1}$),

**Scheme 1.**



**Scheme 2.**




**1**, **2**, R = H, R' = Ph (**a**), $C_6H_4OEt$-4 (**b**), $C_6H_4Cl$-4 (**d**), $C_6H_4Br$-4 (**e**), $C_6H_4OMe$-4 (**f**), $C_6H_4Me$-4 (**g**), OEt (**h**); R = Cl, R' = Ph (**c**), OEt (**i**).

two lactam carbonyl groups $C^4$=O and $C^7$=O, and acyl carbonyl group R'C=O (1663–1694 $cm^{-1}$) are present.

In $^1H$ NMR spectra of compounds **2a–2i** besides the proton signals of aliphatic substituents, aromatic rings, and groups bound with them a broadened singlet of phenol OH group in the 9.79–11.68 ppm region is present.

In $^{13}C$ NMR spectrum of compounds **2a–2g** along with the signals of carbon atoms of aliphatic substituents, aromatic rings, and groups bound with them signals of spiroatom $C^5$ (82.7–82.9 ppm), atom $C^9$ (114.5–117.0 ppm), and of lactam carbonyl group $C^7$=O (154.1–161.7 ppm) of pyrrole fragment, atom $C^2$ (165.1–165.6 ppm) and of lactam carbonyl group $C^4$=O (186.1–187.5 ppm) of thiazole fragment, acyl carbonyl group C(Ar)=O (187.4–187.7 ppm), atom $C^8$ (193.9–194.3 ppm) of pyrrole fragment are present.

In $^{13}C$ NMR spectra of compounds **2h** and **2i** along with the signals of carbon atoms of aliphatic substituents, aromatic rings, and groups bound with them signals of spiroatom $C^5$ (82.7–82.9 ppm), atom $C^9$ (114.5–117.0 ppm) and lactam carbonyl group $C^7$=O (154.1–161.7 ppm) of pyrrol fragment, ester carbonyl group COO (160.9 ppm), atom $C^2$ (165.1–165.6 ppm) and lactam carbonyl group $C^4$=O (186.1–187.5 ppm) of thiazole fragment, atom $C^8$ (193.9–194.3 ppm) of pyrrole fragment are present.

To confirm the structure of obtained compounds XRD analysis of compound **2b** was carried out (see the figure).

According to the XRD data compound **2b** crystallized in centersymmetrical space group of monoclinic crystal system. Lengths of bonds and bond angles are in the range of expected values.

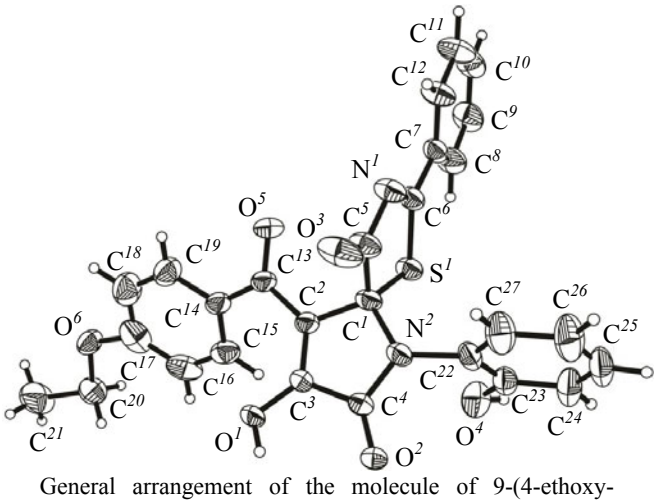
The formation of compounds **2a–2i** evidently occurs as a result of the addition of SH group of thiolimide form of thiobenzamide to the atom $C^{3a}$ of pyrrolediones **1a–1i** followed by the closure of the thiazole ring due to an intramolecular attack of the NH group of thiolimide fragment on the lactone carbonyl group of benzoxazine cycle and its opening at the $C^4$–$O^5$ bond.

Solutions of compounds **2a–2i** colorless at room temperature at heating get violet, and the color intensity increases as temperature grows. Such changes in color may be caused by thermal dissociation of compounds **2a–2i** into initial dark-violet pyrrolediones **1a–1i** and thiobenzamide.

The described reaction is the first example of the synthesis of difficultly accessible heterocyclic system of spiro[thiazolo-5,2'-pyrrole].

## EXPERIMENTAL

$^1H$ and $^{13}C$ NMR spectra were registered on a Bruker Avance III HD 400 spectrometer (400 and




General arrangement of the molecule of 9-(4-ethoxybenzoyl)-8-hydroxy-6-(2-hydroxyphenyl)-2-phenyl-1-thia-3,6-diazaspiro[4.4]nona-2,8-diene-4,7-dione **2b** according to XRD data.

100 MHz correspondingly), internal reference was HMDSO. IR spectra were recorded on a Perkin Elmer Spectrum Two spectrophotometer in mineral oil. Elemental analysis was carried out on a vario Micro cube analyzer. Optimization of reaction conditions was performed by monitoring with $^1$H NMR (on a Bruker Avance III HD 400 instrument) and ultra-HLPC (on an Waters Acquity UPLCI-Class instrument, column Acquity UPLC BEH C18 1.7 μm, mobile phases acetonitrile–water, flow rate 0.6 mL/min, UV detector Acquity UPLC PDA eλ, mass-detector XevoTQD, electrospray ionization, mode of registration of positive ions, ion source temperature 150°C, charge on the capillary 3500–4000 V, charge on the cone 20–70 V, evaporation temperature 150–300°C). Homogeneity of synthesized compounds was confirmed by TLC on Sorbfil and Merck Silica gel 60 $F_{254}$ plates, eluents toluene, ethyl acetate, toluene–ethyl acetate, 5 : 1, spots visualized with iodine vapor and UV irradiation, λ 254 nm. Initial pyrrolediones **1a–1g** were synthesized from the corresponding enamines and oxalyl chloride by methods [9, 10].

**Ethyl 1,2,4-trioxopyrrolo[2,1-*c*][1,4]benzoxazine-3-carboxylate (1h).** A mixture of 1 g (4.3 mmol) of ethyl (2*Z*)-[2-oxo-2*H*-1,4-benzoxazin-3(4*H*)-ylidene]-acetate [11] and 0.82 g (6.5 mmol) of oxalyl chloride was boiled for 110 min in 20 mL of anhydrous chloroform, cooled, and evaporated till dryness in a vacuum. Dry violet precipitate was triturated with anhydrous petroleum ether (bp 40–70°C). Yield 1.11 g (90%), mp 156–157°C (petroleum ether, decomp.). IR spectrum, ν, cm$^{-1}$: 1782, 1740, 1673 ($C^1$=O, $C^5$=O, $C^3$=O), 1625 (COOEt). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.39 m (3H, Me), 4.42 m (2H, $CH_2$), 7.21–7.34 m ($4H_{arom}$). Found, %: C 58.68; H 2.99; N 4.75. $C_{14}H_9NO_6$. Calculated, %: C 58.54; H 3.16; N 4.88.

**Ethyl 8-chloro-1,2,4-trioxopyrrolo[2,1-*c*][1,4]-benzoxazine-3-carboxylate (1i)** was obtained similarly. Yield 1.09 g (92%), mp 93–98°C (petroleum ether, decomp.). IR spectrum, ν, cm$^{-1}$: 1789, 1741, 1681 ($C^1$=O, $C^5$=O, $C^3$=O), 1632 (COOEt). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.39 m (3H, Me), 4.42 m (2H, $CH_2$), 7.14–7.56 m ($3H_{arom}$). Found, %: C 52.39; H 2.66; N 4.20. $C_{14}H_8ClNO_6$. Calculated, %: C 52.28; H 2.51; N 4.35.

**9-Benzoyl-8-hydroxy-6-(2-hydroxyphenyl)-2-phenyl-1-thia-3,6-diazaspiro[4.4]nona-2,8-diene-4,7-dione (2a).** To a suspension of 0.5 g (1.6 mmol) of compound **1a** in 15 mL of anhydrous toluene was added 0.22 g (1.6 mmol) of thiobenzamide, the mixture was boiled for 20 min (till violet color disappeared), cooled, the precipitate was filtered off. Yield 0.59 g (84%), mp 194–195°C (toluene, decomp.). IR spectrum, ν, cm$^{-1}$: 3436 (O–H), 1712, 1697 ($C^4$=O, $C^7$=O), 1674 (COPh). $^1$H NMR spectrum, δ, ppm: 6.78 m ($1H_{arom}$), 6.93 m ($2H_{arom}$), 7.21 m ($1H_{arom}$), 7.50–7.65 m ($5H_{arom}$), 7.74–7.82 m ($3H_{arom}$), 8.00 m ($2H_{arom}$), 9.81 br.s (1H, $OH_{phenol}$). $^{13}$C NMR spectrum, δ, ppm: 82.9 ($C^5$), 114.5 ($C^9$), 116.6, 117.0, 119.4, 120.3, 128.2 (2C), 128.4 (2C), 128.8 (2C), 128.9, 129.5 (2C), 130.8, 131.3, 132.9, 135.9, 137.2, 154.1 ($C_{arom}$), 154.7 ($C^7$), 165.2 ($C^2$), 187.5 ($C^4$), 187.7 (<u>C</u>OPh), 194.2 ($C^8$). Found, %: C 65.69; H 3.63; N 6.20. $C_{25}H_{16}N_2O_5S$. Calculated, %: C 65.78; H 3.53; N 6.14.

Compounds **2b–2i** were synthesized similarly.

**9-(4-Ethoxybenzoyl)-8-hydroxy-6-(2-hydroxy-phenyl)-2-phenyl-1-thia-3,6-diazaspiro[4.4]nona-2,8-diene-4,7-dione (2b).** Yield 0.63 g (82%), mp 198–199°C (toluene, decomp.). IR spectrum, ν, cm$^{-1}$: 3438 (O–H), 1724, 1692 ($C^4$=O, $C^7$=O), 1663 (COAr). $^1$H NMR spectrum, δ, ppm: 1.36 t (3H, $CH_3$, *J* 7.0 Hz), 4.14 q (2H, $OCH_2$, *J* 7.0 Hz), 6.78 m ($1H_{arom}$), 6.91 m ($2H_{arom}$), 7.03 m ($2H_{arom}$), 7.21 m ($1H_{arom}$), 7.57 m ($2H_{arom}$), 7.74–7.83 m ($3H_{arom}$), 7.99 m ($2H_{arom}$), 9.79 br.s ($OH_{phenol}$). $^{13}$C NMR spectrum, δ, ppm: 14.5 ($OCH_2\underline{C}H_3$), 63.6 ($O\underline{C}H_2CH_3$), 82.9 ($C^5$), 113.9 (2C), 117.0 ($C^9$), 117.4, 119.3, 120.4, 128.5 (2C), 128.9, 129.4, 129.5 (2C), 130.8, 131.3, 131.5 (2C), 135.9, 152.5 ($C_{arom}$), 154.7 ($C^7$), 162.7 ($\underline{C}_{arom}OEt$), 165.3 ($C^2$), 186.1 ($C^4$), 187.4 (<u>C</u>OPh), 193.9 ($C^8$). Found, %: C 64.77; H 3.99; N 5.49. $C_{27}H_{20}N_2O_6S$. Calculated, %: C 64.79; H 4.03; N 5.60.

X-ray diffraction (XRD) analysis of compound **2b** was performed on a single crystal diffractometer Xcalibur Ruby [295(2) K, Mo$K_\alpha$-radiation, ω-scanning with a step 1 deg]. The extinction was accounted for empirically using algorythm SCALE3 ABSPACK [12]. Crystal of monoclinic crystal system: *a* 7.2746(13), *b* 18.022(3), *c* 18.036(2) Å, β 95.931(15) deg, *V* 2351.9(6) Å$^3$, space group $P2_1/c$, *Z* 4. The structure was solved with software Superflip [13] and refined by the full-matrix least-squares method in anisotropic approximation for all non-hydrogen atoms with application of software SHELXL-2014 [14] and OLEX2 [15]. Hydrogen atoms of OH groups were refined independently in an isotropic approximation. At refining the other hydrogen atoms the *rider* model

was applied. Final parameters of refinement are as follows: $R_1$ 0.0566, $wR_2$ 0.1373 [for 3634 reflections with $I > 2\sigma(I)$]; $R_1$ 0.0890, $wR_2$ 0.1609 (for all 5520 independent reflections), $S$ 1.016.

Full set of crystallographic data was deposited in Cambridge Crystallographic Data Centre, number CCDC 1830298, and may be requested free by the link: www.ccdc.cam.ac.uk.

**9-Benzoyl-6-(5-chloro-2-hydroxyphenyl)-8-hydroxy-2-phenyl-1-thia-3,6-diazaspiro[4.4]nona-2,8-diene-4,7-dione (2c).** Yield 0.61 g (81%), mp 201–202°C (toluene, decomp.). IR spectrum, ν, $cm^{-1}$: 3236 (O–H), 1744, 1709 ($C^4$=O, $C^7$=O), 1669 (COPh). $^1H$ NMR spectrum, δ, ppm: 6.95 m ($2H_{arom}$), 7.29 m ($1H_{arom}$), 7.50–7.65 m ($5H_{arom}$), 7.76–7.82 m ($3H_{arom}$), 8.03 m ($2H_{arom}$), 10.23 br.s ($OH_{phenol}$). $^{13}C$ NMR spectrum, δ, ppm: 82.7 ($C^5$), 116.8 ($C^9$), 118.6, 121.4, 121.9, 128.2 (2C), 128.6 (2C), 128.7, 128.9 (2C), 129.6 (2C), 130.8, 131.2, 132.9, 136.1, 137.1, 153.9 ($C_{arom}$),154.1 ($C^7$), 165.3 ($C^2$), 187.3 ($C^4$), 187.7 (COPh), 194.3 ($C^8$). Found, %: C 61.21; H 3.04; N 5.79. $C_{25}H_{15}ClN_2O_6S$. Calculated, %: C 61.17; H 3.08; N 5.71.

**9-(4-Chlorobenzoyl)-8-hydroxy-6-(2-hydroxyphenyl)-2-phenyl-1-thia-3,6-diazaspiro[4.4]nona-2,8-diene-4,7-dione (2d).** Yield 0.61 g (81%), mp 198–199°C (toluene, decomp.). IR spectrum, ν, $cm^{-1}$: 3515 (O–H), 1747, 1690 ($C^4$=O, $C^7$=O), 1674 (COAr). $^1H$ NMR spectrum, δ, ppm: 6.78 m ($1H_{arom}$), 6.91 m ($2H_{arom}$), 7.21 m ($1H_{arom}$), 7.55–7.61 m ($4H_{arom}$), 7.75–7.83 m ($3H_{arom}$), 8.00 m ($2H_{arom}$), 9.84 br.s ($OH_{phenol}$). $^{13}C$ NMR spectrum, δ, ppm: 82.8 ($C^5$), 116.0 ($C^9$), 117.0, 119.4, 120.3, 128.3 (2C), 128.5 (2C), 128.9, 129.5 (2C), 130.7 (2C), 130.8, 131.2, 135.9, 136.0, 137.7, 154.7 ($C_{arom}$), 154.9 ($C^7$), 165.1 ($C^2$), 186.4 ($C^4$), 187.5 (COPh), 194.3 ($C^8$). Found, %: C 61.19; H 3.11; N 5.66. $C_{25}H_{15}ClN_2O_6S$. Calculated, %: C 61.17; H 3.08; N 5.71.

**9-(4-Bromobenzoyl)-8-hydroxy-6-(2-hydroxyphenyl)-2-phenyl-1-thia-3,6-diazaspiro[4.4]nona-2,8-diene-4,7-dione (2e).** Yield 0.69 g (83%), mp 189–190°C (toluene, decomp.). IR spectrum, ν, $cm^{-1}$: 3516 (O–H), 1746, 1699 ($C^4$=O, $C^7$=O), 1673 (COAr). $^1H$ NMR spectrum, δ, ppm: 6.78 m ($1H_{arom}$), 6.92 m ($2H_{arom}$), 7.21 m ($1H_{arom}$), 7.57 m ($2H_{arom}$), 7.71–7.79 m ($5H_{arom}$), 8.00 m ($2H_{arom}$), 9.80 br.s ($OH_{phenol}$). $^{13}C$ NMR spectrum, δ, ppm: 82.8 ($C^5$), 116.0 ($C^9$), 117.0, 119.3, 120.3, 126.7, 128.5 (2C), 128.8, 129.0, 129.5 (2C), 130.8, 130.8 (2C), 131.3 (2C), 135.9, 136.4, 154.7 ($C_{arom}$), 155.1 ($C^7$), 165.1 ($C^2$), 186.5 ($C^4$), 187.5 (COPh), 194.3 ($C^8$). Found, %: C 56.11; H 2.77; N 5.30. $C_{25}H_{15}BrN_2O_6S$. Calculated, %: C 56.09; H 2.82; N 5.23.

**8-Hydroxy-6-(2-hydroxyphenyl)-9-(4-methoxybenzoyl)-2-phenyl-1-thia-3,6-diazaspiro[4.4]nona-2,8-diene-4,7-dione (2f).** Yield 0.61 g (81%), mp 187–188°C (toluene, decomp.). IR spectrum, ν, $cm^{-1}$: 3503 (O–H), 1748, 1694 ($C^4$=O, $C^7$=O), 1675 (COAr). $^1H$ NMR spectrum, δ, ppm: 3.87 s (3H, Me), 6.77 m ($1H_{arom}$), 6.91 m ($2H_{arom}$), 7.06 m ($2H_{arom}$), 7.21 m ($1H_{arom}$), 7.57 m ($2H_{arom}$), 7.73–7.78 m ($1H_{arom}$), 7.81–7.85 m ($2H_{arom}$), 7.99 m ($2H_{arom}$), 9.80 br.s ($OH_{phenol}$). $^{13}C$ NMR spectrum, δ, ppm: 55.6 ($OCH_3$), 82.9 ($C^5$), 113.6 (2C), 117.0 ($C^9$), 117.4, 119.4, 120.4, 128.5 (2C), 128.9, 129.5 (2C), 129.6, 130.8, 131.3, 131.5 (2C), 135.9, 152.6 ($C_{arom}$), 154.7 ($C^7$), 163.3 ($C_{arom}$OMe), 165.3 ($C^2$), 186.1 ($C^4$), 187.4 (COPh), 194.0 ($C^8$). Found, %: C 64.20; H 3.77; N 5.70. $C_{26}H_{18}N_2O_6S$. Calculated, %: C 64.14; H 3.72; N 5.75.

**8-Hydroxy-6-(2-hydroxyphenyl)-9-(4-methylbenzoyl)-2-phenyl-1-thia-3,6-diazaspiro[4.4]nona-2,8-diene-4,7-dione (2g).** Yield 0.63 g (87%), mp 203–205°C (toluene, decomp.). IR spectrum, ν, $cm^{-1}$: 3352 (O–H), 1731, 1704 ($C^4$=O, $C^7$=O), 1679 (COAr). $^1H$ NMR spectrum, δ, ppm: 2.40 s (3H, $CH_3$), 6.78 m ($1H_{arom}$), 6.93 m ($2H_{arom}$), 7.21 m ($1H_{arom}$), 7.33 m (2H, $H_{arom}$), 7.57 m ($2H_{arom}$), 7.71–7.78 m ($3H_{arom}$), 8.00 m ($2H_{arom}$), 9.80 br.s ($OH_{phenol}$). $^{13}C$ NMR spectrum, δ, ppm: 21.2 ($CH_3$), 82.8 ($C^5$), 117.0 ($C^9$), 119.4, 120.3, 120.3, 128.4 (2C), 128.8 (2C), 128.9, 129.0, 129.1 (2C), 129.5 (2C), 130.8, 131.3, 134.5, 135.9, 143.5, 153.4 ($C_{arom}$), 154.7 ($C^7$), 165.2 ($C^2$), 187.3 ($C^4$), 187.4 (COPh), 194.2 ($C^8$). Found, %: C 66.35; H 3.89; N 5.92. $C_{26}H_{18}N_2O_5S$. Calculated, %: C 66.37; H 3.86; N 5.95.

**Ethyl 8-hydroxy-6-(2-hydroxyphenyl)-4,7-dioxo-2-phenyl-1-thia-3,6-diazaspiro[4.4]nona-2,8-diene-9-carboxylate (2h).** Yield 0.57 g (84%), mp 190–192°C (toluene, decomp.). IR spectrum, ν, $cm^{-1}$: 3287 (O–H), 1728, 1713 ($C^4$=O, $C^7$=O), 1694 (COOEt). $^1H$ NMR spectrum, δ, ppm: 1.08 t (3H, Me, $J$ 7.1 Hz), 4.11 m (2H, $CH_2$), 6.76 m ($1H_{arom}$), 6.87–6.90 m ($2H_{arom}$), 7.17–7.21 m ($1H_{arom}$), 7.59 m ($2H_{arom}$), 7.78 m ($1H_{arom}$), 7.99–8.02 m ($2H_{arom}$), 9.81 br.s ($OH_{phenol}$). $^{13}C$ NMR spectrum, δ, ppm: 13.9 (Me), 60.3 ($CH_2$), 82.4 ($C^5$), 108.8 ($C^9$), 117.0, 119.3, 120.3, 128.5 (2C), 129.0, 129.6 (2C), 130.8, 131.3, 136.2, 154.6 ($C_{arom}$), 155.6 ($C^7$), 160.9 (COOEt), 164.3 ($C^2$), 187.2 ($C^4$), 195.5

($C^8$). Found, %: C 59.45; H 3.83; N 6.62. $C_{21}H_{16}N_2O_6S$. Calculated, %: C 59.43; H 3.80; N 6.60.

**Ethyl 6-(5-chloro-2-hydroxyphenyl)-8-hydroxy-4,7-dioxo-2-phenyl-1-thia-3,6-diazaspiro[4.4]nona-2,8-diene-9-carboxylate (2i).** Yield 0.62 g (85%), mp 183–185°C (toluene, decomp.). IR spectrum, ν, $cm^{-1}$: 3264 (O–H), 1738, 1715 ($C^4$=O, $C^7$=O), 1691 (COOEt). $^1$H NMR spectrum, δ, ppm: 1.08 t (3H, Me, *J* 7.1 Hz), 4.11 m (2H, $CH_2$), 6.92 m ($2H_{arom}$), 7.27 m ($1H_{arom}$), 7.59–7.63 m ($2H_{arom}$), 7.81 m ($1H_{arom}$), 8.05 m ($2H_{arom}$), 10.22 br.s ($OH_{phenol}$). $^{13}$C NMR spectrum, δ, ppm: 13.9 (Me), 60.4 ($CH_2$), 82.2 ($C^5$), 108.8 ($C^9$), 118.6, 121.3, 121.9, 128.6 (2C), 128.8, 129.6 (2C), 130.8, 131.2, 136.3, 153.9 ($C_{arom}$), 155.5 ($C^7$), 160.9 (COOEt), 164.4 ($C^2$), 187.0 ($C^4$), 195.5 ($C^8$). Found, %: C 54.97; H 3.30; N 6.11. $C_{21}H_{15}ClN_2O_6S$. Calculated, %: C 54.95; H 3.32; N 6.13.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Mashkovskii, M.D., *Lekarstvennye sredstva* (Drugs), Moscow: Novaya Volna, 2010.
2. Hulin, B., McCarthy, P.A., and Gibbs, E.M., *Curr. Pharm. Des*., 1996, vol. 2, p. 85.
3. Breslow, R., *J. Am. Chem. Soc*., 1958, vol. 80, p. 3719.
4. Meroni, G., Rajabi, M., and Santaniello, E., *Arkivoc*, 2009, p. 265.
5. Racheva, N.L., Aliev, Z.G., Belova, M.A., Mashevskaya, I.V., and Maslivets, A.N., *Russ. J. Org. Chem*., 2008, vol. 44, p. 701. doi 10.1134/S1070428008050114
6. Bubnov, N.V., Denislamova, E.S., Aliev, Z.G., and Maslivets, A.N., *Russ. J. Org. Chem*., 2010, vol. 46, p. 1891. doi 10.1134/S1070428010120201
7. Babenysheva, A.V., Maslivets, V.A., and Maslivets, A.N., *Russ. J. Org. Chem*., 2007, vol. 43, p. 1577. doi 10.1134/S107042800710034X
8. Kobelev, A.I., Stepanova, E.E., Dmitriev, M.V., and Maslivets, A.N., *Russ. J. Org. Chem*., 2016, vol. 52, p. 1363. doi 10.1134/S1070428016090219
9. Maslivets, A.N., Mashevskaya, I.V., Smirnova, L.I., Krasnykh, O.P., Shurov, S.N., and Andreichikov, Yu.S., *Zh. Org. Khim*., 1992, vol. 28, p. 2545.
10. Stepanova, E.E., Babenysheva, A.V., and Maslivets, A.N., *Russ. J. Org. Chem*., 2011, vol. 47, p. 937. doi 10.1134/S1070428011060182
11. Babenysheva, A.V., Lisovskaya, N.A., Belevich, I.O., and Lisovenko, N.Yu., *Pharm. Chem. J*., 2006, vol. 40, p. 611. doi 10.1007/s11094-006-0204-6
12. *CrysAlisPro*, Agilent Technologies, Version 1.171.37.33 (release 27-03-2014 CrysAlis171.NET).
13. Palatinus, L. and Chapuis, G., *J. Appl. Cryst*., 2007, vol. 40, p. 786.
14. Sheldrick, G.M., *Acta Cryst. Sect. C*, 2015, vol. 71, p. 3.
15. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K., and Puschmann, H., *J. Appl. Cryst*., 2009, vol. 42, p. 339.