ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 5, pp. 701–705. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © N.L. Racheva, Z.G. Aliev, M.A. Belova, I.V. Mashevskaya, A.N. Maslivets, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 5, pp. 710–714.

Five-Membered 2,3-Dioxoheterocycles: LIX.* Reaction of 3-Aroyl-1*H*-pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-triones with Acyclic β-Enaminoesters. Crystal and Molecular Structure of Ethyl 3-Benzoyl-4-hydroxy-1-*o*-hydroxyphenyl-5-oxo-2,3-dihydro-1*H*-pyrrolo-2-spiro-3'-(5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrolo-4-carboxylate)

N. L. Racheva[a], Z. G. Aliev[b], M. A. Belova[a], I. V. Mashevskaya[a], and A. N. Maslivets[a]

[a]*Perm State University, Perm, 614990 Russia*
e-mail: koh2@psu.ru
[b]*Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Russia*

Received June 15, 2006

Abstract—3-Aroyl-1*H*-pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-triones react with substituted alkyl 3-amino-2-propenoates to form substituted alkyl 3-aroyl-4-hydroxy-1-*o*-hydroxyphenyl-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-(2-oxo-2,3-dihydro-1*H*-pyrrole-4-carboxylates). Crystal and molecular structure of ethyl 3-benzoyl-4-hydroxy-1-*o*-hydroxyphenyl-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-(5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-4-carboxylate) was investigated.

DOI: 10.1134/S1070428008050114

The transformations of 4-acyl-1*H*-pyrrole-2,3-diones, among them those fused at the [*a*] side to azaheterocycles (hetereno[*a*]pyrrole-2,3-diones), under treatment with binucleophilic reagents are used for designing versatile fused heterocyclic systems [2, 3].

We showed formerly that 4-acyl-1*H*-pyrrole-2,3-diones fused to 1,4-benzoxazine ring, 3-aroyl-1*H*-pyrrolo[2,1-*c*][1,4]-benzoxazine-1,2,4-triones **Ia–Ic**, reacted with acyclic enaminoketones as with 1,3-CH,NH-binucleophiles by a pathroute involving a consecutive attacks by the β-CH and NH groups of enaminoketone on carbon atoms in positions *3a* and *4* respectively of pyrrolobenzoxazinetriones. The reaction includes a cleavage of the benzoxazine ring of pyrrolobenzoxazinetriones at the C^4–O^5 bond and results in the formation of substituted 3-aroyl-4-hydroxy-1-*o*-hydroxy-phenyl-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-(2-oxo-2,3-dihydro-1*H*-pyrroles) [4].

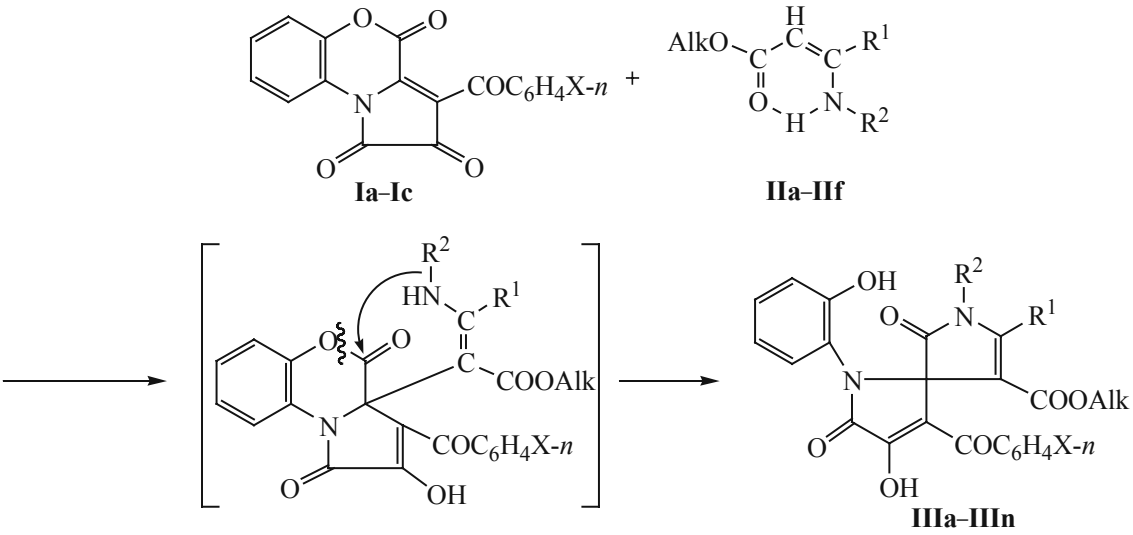
In extension of the investigation of reactions between hetereno[*a*]pyrrole-2,3-diones and binucleophiles we investigated reactions of 3-aroyl-1*H*-pyrrolo-[2,1-*c*]-[1,4]benzoxazine-1,2,4-triones **Ia–Ic** with potential 1,3-CH,NH- binucleophiles β-enaminoesters, substituted alkyl 3-amino2-propenoates **IIa–IIf**: ethyl (2*Z*)-3-amino-2-butenoate (**IIa**), ethyl (2*Z*)-3-anilino-2-butenoate (**IIb**), ethyl (2*Z*)-3-(4-toluidino)-2-butenoate (**IIc**), ethyl (*Z*)-3-(4-methoxyanilino)-2-butenoate (**IId**), ethyl (*Z*)-3-(4-chloroanilino)-2-butenoate (**IIe**), and propyl (2*Z*)-3-amino-3-(4-pyridinyl)-2-propenoate (**IIf**).

The reaction of equimolar amounts of pyrrolobenzoxazinetriones **Ia–Ic** and substituted alkyl 3-amino2-propenoates **IIa–IIf** at boiling in anhydrous benzene for 5–7 min led to the formation in high yields of substituted alkyl 3-aroyl-4-hydroxy-1-*o*-hydroxy-phenyl-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-(2-oxo-2,3-dihydro-1*H*-pyrrole-4-carboxylates) **IIIa–IIIn**.**

Compounds **IIIa–IIIn** are colorless or light-yellow crystalline substances melting at high temperature with decomposition, readily soluble in DMF and DMSO, sparingly soluble in common organic solvents, insoluble

* For communication LVIII, see [1].

** For preliminary communication, see [5].



Ia–Ic **IIa–IIf** **IIIa–IIIn**

I, X = H (**a**), OMe (**b**), Br (**c**); **II**, Alk = Et, R^1 = Me, R^2 = H (**a**), Ph (**b**), C_6H_4Me-*p* (**c**), C_6H_4OMe-*p* (**d**), C_6H_4Cl-*p* (**e**); Alk = *iso*-C_3H_7, R^1 = β-pyridyl, R^2 = H (**f**); **III**, Alk = Et, R^1 = Me: X = H, R^2 = H (**a**), Ph (**b**), C_6H_4Me-*p* (**e**), C_6H_4OMe-*p* (**h**), C_6H_4Cl-*n* (**k**); X = OMe, R^2 = Ph (**c**), C_6H_4Me-*n* (**f**),C_6H_4OMe-*p* (**i**), C_6H_4Cl-*p* (**l**); X = Br, R^2 = Ph (**d**), C_6H_4Me-*p* (**g**), C_6H_4OMe-*p* (**j**), C_6H_4Cl-*p* (**m**); X = R^2 = H, Alk = *iso*-C_3H_7, R^1 = β-pyridyl (**n**).

in alkanes and water, positive test with iron(III) chloride on the presence of enol and phenol hydroxy group (cherry-red coloration).

The IR spectra of spiro-compounds **IIIa–IIIn** contain the bands of the stretching vibrations of OH groups as a broad peak in the region 3156–3231 cm^{-1}, of ethoxycarbonyl (in compounds **IIIa–IIIm**) and isopropoxycarbonyl (in compound **IIIn**) groups in the region 1752–1765 cm^{-1}, of two lactam carbonyl groups as one or two peaks in the region 1700–1746 cm^{-1}, of aroyl carbonyl in the region 1619–1651 cm^{-1} (in compounds **IIIa–IIIm**) and at 1692 cm^{-1} (in compound **IIIn**).

In the ^1H NMR spectra of solutions of spiro-compounds **IIIa–IIIn** in DMSO-d_6 alongside the signals of aromatic rings protons and of the groups attached thereto appear a triplet and a quartet of the protons from ethoxycarbonyl group in the region 1.18–1.22 and 4.02–4.06 ppm respectively (in compounds **IIIa–IIIm**), a doublet and multiplet of the protons from isopropoxycarbonyl group at 1.04 and 4.75 ppm respectively (in compound **IIIn**), a singlet of protons of a methyl group in the position *5* of the 2,3-dihydro-1*H*-pyrrole ring in the region 1.99–2.14 ppm (in compounds **IIIa–IIIm**), a singlet of phenol hydroxy group in the region 9.62–

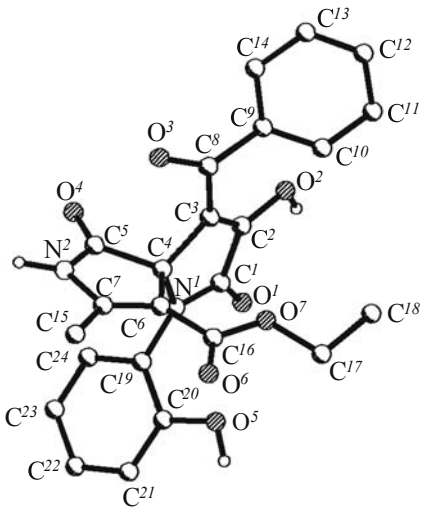


Fig. 1. General view of ester molecule **IIIa**

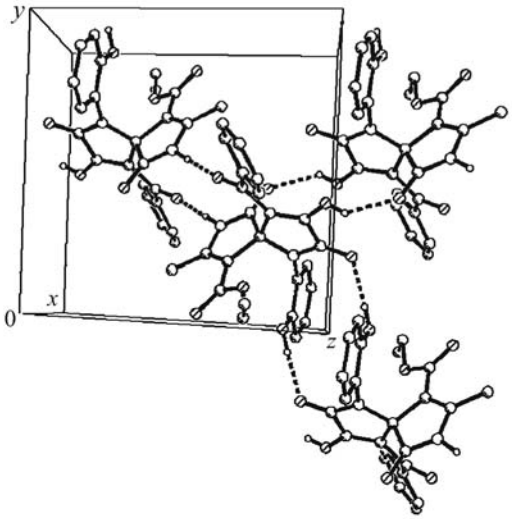


Fig. 2. Hydrogen bonds in **IIIa** molecule.

Parameters of hydrogen bonds in the molecule of ethyl 3-benzoyl-4-hydroxy-1-(*o*-hydroxyphenyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-(5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-4-carboxylate) (**IIIa**) (bonds, Å, angles, deg)

Atoms	*D*–H	H···*A*	*D*···*A*	angle *DHA*	Group
O^5–H^5···O^1	0.88(9)	1.88(9)	2.749(5)	170(8)	2 – *x*, –*y*, 2 – *z*
O^2–H^2···O^4	0.77(7)	2.02(7)	2.630(6)	137(6)	2 – *x*, 1 – *y*, 2 – *z*
N^2–H^{2A}···O^3	1.04(6)	1.79(6)	2.833(6)	173(5)	2 – *x*, 1 – *y*, 1 – *z*

10.00 ppm, a singlet from NH gpoup at 10.66–11.00 ppm (in compounds **IIIa** and **IIIn**), and broad singlet of the enol OH group in the region 12.00–12.82 ppm.

As showed XRD analysis compound **IIIa** crystallized with a molecule of ethyl acetate in an equimolar ratio. All the bond distances and bond angles in the molecule (Fig. 1) are in the range common to the corresponding atoms. In the crystal the molecule forms two hydrogen bonds with each of three contiguous molecules; these three molecules are united with the first one through a center of symmetry (Fig. 2). Parameters of the hydrogen bonds are given in the table. The observed distances *D*···*A* indicate that the hydrogen bonds are sufficiently strong, especially the bond O^2–H^2···O^4. The involvement into the hydrogen bond is adequately reflected in the interatomic distances C–O in carboxy and carbonyl groups (see the table).

Evidently in the first stage of the reaction the activated β-CH group of the enamino fragment of β-enaminoesters **IIa–IIf** adds to the carbon atom in the position *3a* of pyrrolobenzoxazinetriones **Ia–Ic** as is described for the reactions of these compounds with mononucleophiles [2, 3]; further a pyrrole ring closes by intramolecular attack of the free amino group of the side chain of enaminoesters **IIa–IIf** on the lactone carbonyl group of the benzoxazine ring of compounds **Ia–Ic** with the opening of the ring at the C^4–O^5 bond. The described reaction is a rare example of building up a difficultly accessible spiro-bis-heterocyclic system pyrrole-spiro-pyrrole with purposefully variable functional substituents in several positions of both pyrrole rings.

EXPERIMENTAL

IR spectra of compounds synthesized were recorded on a spectrophotometer FSM-1201 from mills in mineral oil. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker AM-400 (operating frequency 400 MHz) from solutions in DMSO-d_6, internal reference TMS. The homogeneity of compounds synthesized was checked by TLC on Silufol plates, eluents ethyl acetate, ethyl acetate–benzene, 1:5, development in iodine vapor.

Ethyl 3-benzoyl-4-hydroxy-1-(*o*-hydroxyphenyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-(5-methyl-2-oxo-2,3-dihydro-1*H*-pyrrole-4-carboxylate) (IIIa). A solution of 1.0 mmol of compound **Ia** and 1.0 mmol of enamine **IIa** in 10 ml of anhydrous benzene was boiled for 3 min, cooled, the separated precipitate was filtered off. Yield 82%, mp 257–259°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3160 br (OH), 1755 (COOEt), 1700, 1680 (C^2=O, C^5=O), 1640 (COPh). ^{1}H NMR spectrum, δ, ppm: 1.18 t (3H, CH_3CH_2, *J* 6.8 Hz), 2.14 s (3H, Me), 4.04 q (2H, CH_3CH_2, *J* 7.3 Hz), 6.75–7.74 group of signals (9H, Ph + C_6H_4), 9.62 s (1H, OH phenol), 10.66 s (1H, NH), 12.00 br.s (1H, OH enol). Found, %: C 64.31; H 4.53; N 6.12. $C_{24}H_{20}N_2O_7$. Calculated, %: C 64.27; H 4.49; N 6.26.

Compounds **IIIb–IIIn** were similarly synthesized.

Ethyl 3-benzoyl-4-hydroxy-1-(*o*-hydroxyphenyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-(5-methyl-2-oxo-1-phenyl-2,3-dihydro-1*H*-pyrrole-4-carboxylate) (IIIb). Yield 80%, mp 212–215°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3164 br (OH), 1753 (COOEt), 1707, 1656 (C^2=O, C^5=O), 1632 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.22 t (3H, CH_3CH_2, *J* 6.8 Hz), 2.04 s (3H, Me), 4.04 q (2H, CH_3CH_2, *J* 7.3 Hz), 6.81–7.81 group of signals (14H, 2Ph + C_6H_4), 9.82 s (1H, OH phenol), 12.40 br.s (1H, OH enol). Found, %: C 68.64; H 4.69; N 5.26. $C_{30}H_{24}N_2O_7$. Calculated, %: C 68.70; H 4.61; N 5.34.

Ethyl 4-hydroxy-1-(*o*-hydroxyphenyl)-3-(*p*-methoxybenzoyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-(5-methyl-2-oxo-1-phenyl-2,3-dihydro-1*H*-pyrrole-4-carboxylate) (IIIc). Yield 87%, mp 203–205°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3158 br (OH), 1753 (COOEt), 1705, 1657 (C^2=O, C^5=O), 1619 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.21 t (3H, CH_3CH_2, *J* 7.4 Hz), 2.04 s (3H, Me), 3.86 s (1H, OMe), 4.04 q (2H, CH_3CH_2, *J* 7.1 Hz), 6.81–7.83 group of signals (13H, Ph + 2C_6H_4), 9.81 s (1H, OH phenol), 12.16 br.s

(1H, OH enol). Found, %: C 67.20; H 4.89; N 5.03. $C_{31}H_{26}N_2O_8$. Calculated, %: C 67.14; H 4.73; N 5.05.

Ethyl 3-*p*-bromobenzoyl-4-hydroxy-1-(*o*-hydroxyphenyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-(5-methyl-2-oxo-1-phenyl-2,3-dihydro-1*H*-pyrrole-4-carboxylate) (IIId). Yield 90%, mp 211–213°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3156 br (OH), 1752 (COOEt), 1707, 1655 (C^2=O, C^5=O), 1628 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.21 t (3H, CH_3CH_2, *J* 7.0 Hz), 2.04 s (3H, Me), 4.06 q (2H, CH_3CH_2, *J* 7.1 Hz), 6.82–7.79 group of signals (13H, Ph + $2C_6H_4$), 9.84 s (1H, OH phenol), 12.60 br.s (1H, OH enol). Found, %: C 59.87; H 3.96; Br 13.39; N 4.60. $C_{30}H_{23}BrN_2O_7$. Calculated, %: C 59.71; H 3.84; Br 13.24; N 4.64.

Ethyl 3-benzoyl-4-hydroxy-1-(*o*-hydroxyphenyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-[5-methyl-2-oxo-1-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrole-4-carboxylate] (IIIe). Yield 89%, mp 221–223°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3191 br (OH), 1755 (COOEt), 1707, 1655 (C^2=O, C^5=O), 1628 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.22 t (3H, CH_3CH_2, *J* 7.0 Hz), 2.03 s (3H, Me), 2.37 s (3H, C_6H_4Me-*p*), 4.05 q (2H, CH_3CH_2, *J* 7.4 Hz), 6.81–7.82 group of signals (13H, Ph + $2C_6H_4$), 9.82 s (1H, OH phenol), 12.35 br.s (1H, OH enol). Found, %: C 69.33; H 4.81; N 5.15. $C_{31}H_{26}N_2O_7$. Calculated, %: C 69.14; H 4.87; N 5.20.

Ethyl 4-hydroxy-1-(*o*-hydroxyphenyl)-3-(*p*-methoxybenzoyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-[5-methyl-2-oxo-1-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrole-4-carboxylate] (IIIf). Yield 96%, mp 198–199°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3180 br (OH), 1753 (COOEt), 1703, 1675 (C^2=O, C^5=O), 1651 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.20 t (3H, CH_3CH_2, *J* 7.1 Hz), 2.01 s (3H, Me), 2.37 s (3H, C_6H_4Me-*p*), 3.86 s (3H, OMe), 4.04 q (2H, CH_3CH_2, *J* 7.4 Hz), 6.80–7.84 group of signals (12H, $3C_6H_4$), 9.78 s (1H, OH phenol), 12.13 br.s (1H, OH enol). Found, %: C 67.69; H 5.08; N 5.05. $C_{32}H_{28}N_2O_8$. Calculated, %: C 67.60; H 4.96; N 4.93.

Ethyl 3-(*p*-bromobenzoyl)-4-hydroxy-1(*o*-hydroxyphenyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-[5-methyl-2-oxo-1-(*p*-toluene)-2,3-dihydro-1*H*-pyrrole-4-carboxylate] (IIIg). Yield 90%, mp 199–202°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3189 br (OH), 1754 (COOEt), 1705, 1656 (C^2=O, C^5=O), 1628 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.20 t (3H, CH_3CH_2, *J* 7.0 Hz), 2.03 s (3H, Me), 2.36 s (3H, C_6H_4Me-*p*), 4.04 q (2H, CH_3CH_2, *J* 7.1 Hz), 6.81–7.79 group of signals (12H, $3C_6H_4$), 9.82 C (1H, OH phenol), 12.60 br.s (1H, OH enol). Found, %: C 60.46; H 4.28; Br 12.95; N 4.51. $C_{31}H_{25}BrN_2O_7$. Calculated, %: C 60.30; H 4.08; Br 12.94; N 4.54.

Ethyl 3-benzoyl-4-hydroxy-1-(*o*-hydroxy-phenyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-[5-methyl-1-(*p*-methoxyphenyl)-2-oxo-2,3-dihydro-1*H*-pyrrole-4-carboxylate] (IIIh). Yield 93%, mp 228–230°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3180 br (OH), 1759 (COOEt), 1737, 1667 (C^2=O, C^5=O), 1637 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.21 t (3H, CH_3CH_2, *J* 7.3 Hz), 2.02 s (3H, Me), 3.81 s (3H, OMe-*p*), 4.05 q (2H, CH_3CH_2, *J* 7.2 Hz), 6.81–7.81 group of signals (13H, Ph + $2C_6H_4$), 9.81 C (1H, OH phenol), 12.30 br.s (1H, OH enol). Found, %: C 67.44; H 4.54; N 5.14. $C_{31}H_{26}N_2O_8$. Calculated, %: C 67.14; H 4.73; N 5.05.

Ethyl 4-hydroxy-1-(*o*-hydroxyphenyl)-3-(*p*-methoxybenzoyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-[5-methyl-1-(*p*-methoxyphenyl)-2-oxo-2,3-dihydro-1*H*-pyrrole-4-carboxylate] (IIIi). Yield 89%, mp 210–212°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3186 br (OH), 1765 (COOEt), 1735, 1698 (C^2=O, C^5=O), 1630 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.21 t (3H, CH_3CH_2, *J* 7.2 Hz), 2.01 s (3H, Me), 3.73 s (3H, OMe-*p*), 3.81 s (3H, OMe-*p*), 4.02 q (2H, CH_3CH_2, *J* 7.2 Hz), 6.80–7.82 group of signals (12H, $3C_6H_4$), 9.79 C (1H, OH phenol), 12.20 br.s (1H, OH enol). Found, %: C 65.63; H 4.90; N 4.69. $C_{32}H_{28}N_2O_9$. Calculated, %: C 65.75; H 4.83; N 4.79.

Ethyl 3-(*p*-bromobenzoyl)-4-hydroxy-1-(*o*-hydroxyphenyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-[5-methyl-1-(*p*-methoxyphenyl)-2-oxo-2,3-dihydro-1*H*-pyrrole-4-carboxylate] (IIIj). Yield 90%, mp 206–208°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3180 br (OH), 1754 (COOEt), 1701, 1672 (C^2=O, C^5=O), 1639 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.21 t (3H, CH_3CH_2, *J* 7.1 Hz), 2.03 s (3H, Me), 3.81 s (3H, OMe-*p*), 4.05 q (2H, CH_3CH_2, *J* 7.1 Hz), 6.80–7.80 group of signals (12H, $3C_6H_4$), 9.85 C (1H, OH phenol), 12.60 br.s (1H, OH enol). Found, %: C 58.70; H 4.00; Br 12.71; N 4.33. $C_{31}H_{25}BrN_2O_8$. Calculated, %: C 58.78; H 3.98; Br 12.61; N 4.42.

Ethyl 3-benzoyl-4-hydroxy-1-(*o*-hydroxy-phenyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-[5-methyl-2-oxo-1-(*p*-chlorophenyl)-2,3-dihydro-1*H*-pyrrole-4-carboxylate] (IIIk). Yield 91%, mp 179–180°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3187 br (OH), 1754 (COOEt), 1698, 1667 (C^2=O, C^5=O), 1636 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.21 t (3H, CH_3CH_2, *J* 7.0 Hz), 2.06 s (3H, Me), 4.05 q (2H, CH_3CH_2,

J 7.1 Hz), 6.80–7.80 group of signals (13H, Ph + $2C_6H_4$), 9.80 s (1H, OH phenol), 12.40 br.s (1H, OH enol). Found, %: C 64.29; H 4.21; Cl 6.23; N 5.19. $C_{30}H_{23}ClN_2O_7$. Calculated, %: C 64.46; H 4.15; Cl 6.34; N 5.01.

Ethyl 4-hydroxy-1-(*o*-hydroxyphenyl)-3-(*p*-methoxybenzoyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-[5-methyl-2-oxo-1-(*p*-chlorophenyl)-2,3-dihydro-1*H*-pyrrole-4-carboxylate] (IIIl). Yield 89%, mp 203–205°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3180 br (OH), 1759 (COOEt), 1699, 1673 (C^2=O, C^5=O), 1632 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.21 t (3H, CH_3CH_2, *J* 7.1 Hz), 2.06 s (3H, Me), 4.03 q (2H, CH_3CH_2, *J* 7.1 Hz), 6.80–7.81 group of signals (12H, $3C_6H_4$), 9.83 s (1H, OH phenol), 12.20 br.s (1H, OH enol). Found, %: C 63.42; H 4.44; Cl 5.98; N 4.67. $C_{31}H_{25}ClN_2O_8$. Calculated, %: C 63.22; H 4.28; Cl 6.02; N 4.76.

Ethyl 3-(*p*-bromobenzoyl)-4-hydroxy-1-(*o*-hydroxyphenyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-spiro-3'-[5-methyl-2-oxo-1-(*p*-chlorophenyl)-2,3-dihydro-1*H*-pyrrole-4-carboxylate] (IIIm). Yield 95%, mp 262–264°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3188 br (OH), 1754 (COOEt), 1726 (C^2=O, C^5=O), 1649 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.20 t (3H, CH_3CH_2, *J* 7.1 Hz), 1.99 s (3H, Me), 4.04 q (2H, CH_3CH_2, *J* 7.1 Hz), 6.80–8.00 group of signals (12H, $3C_6H_4$), 9.93 s (1H, OH phenol), 12.82 br.s (1H, OH enol). Found, %: C 56.57; H 3.38; Br 12.43; Cl 5.38; N 4.33. $C_{30}H_{22}BrClN_2O_7$. Calculated, %: C 56.49; H 3.48; Br 12.53; Cl 5.56; N 4.39.

Isopropyl 3-benzoyl-4-hydroxy-1-(*o*-hydroxyphenyl)-5-oxo-2,5-dihydro-1*H*-pyrrolo-2-spiro-3'-[2-oxo-5-(3-pyridyl)-2,3-dihydro-1*H*-pyrrole-4-carboxylate] (IIIn). Yield 89%, mp 214–216°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3231 br (OH), 1765 (COOPr-*i*), 1746, 1717 (C^2=O, C^5=O), 1692 (COAr). ^{1}H, δ, ppm: 1.04 d (6H, 2Me), 4.75 m (1H, $CHMe_2$), 6.80–8.65 group of signals (13H, Ph + $2C_6H_4$), 9.70 s (1H, OH phenol), 11.00 s (1H, NH), 12.30 br.s (1H, OH enol). Found, %: C 66.47; H 4.22; N 8.15. $C_{29}H_{23}N_3O_7$. Calculated, %: C 66.28; H 4.41; N 8.00.

XRD analysis of compound IIIa. Crystals $C_{24}H_{20}N_2O_7$ triclinic: *a* 10.878(2), *b* 9.995(2), *c* 10.722(2) Å, α 89.58(3), β 108.50(3), γ 94.08(3)°, *V* 1102.6(4) $Å^3$, *M* 448.42, d_{calc} 1.351 g/cm^3, *Z* 2, space group P-1. The set of experimental reflections was obtained on an automatic four-circle diffractometer QM-4 with a ч-geometry, ω/2Θ scanning, monochromated MOK_α-emission (2Θ ≤ 52°). Overall 3209 independent reflections were measured (R_{int} 0.1071). No correction for extinction was done (μ 0.101 mm^{-1}). The structure was solved by the direct method using SIR92 software [6] with subsequent calculations of a series of electron density charts. All hydrogen atoms except those of the methyl of ethoxycarbonyl group were revealed fron the difference synthesis of the electron density. Full-matrix anisotropic (for nonhydrogen atoms) refinement by least-squares method applying SHELXL-97 program [7] was finished at R_1 0.0817 for 1904 reflections with $I \geq 2\sigma(I)$, GOOF 0.972.

The study was carried out under financial support of the Russian Foundation for Basic Research (grants nos. 07-03-96036, 04-03-33024).

REFERENCES

1. Bannikova, Yu.N., Rozhkova, Yu.S., Shklyaev, Yu.V. and Maslivets, A.N., *Zh. Org Khim.,* 2008, vol. 44, no. 4, p. 555.
2. Maslivets, A.N. and Mashevskaya, I.V., *2,3-Digidro-2,3-pirrol-diony* (2,3-Dihydro-2,3-Pyrrolediones), Perm: Izd. Perm. Gos. Univ., 2005, p. 126.
3. Mashevskaya, I.V. and Maslivets, A.N., *2,3-Digidro-2,3-pirrol-diony kondensirovannye s razlichnymi geterotsiklami storonoi [a] i ikh benzo[b]analogi: sintez khimicheskie svoistva prakticheskoe primenenie* (2,3-Dihydro-2,3-pyrroldiones Fused with Various Heterocycles by [*a*] Side, and Their Benzol [*b*] Analogs: Synthesis, Chemical Properties and Practical Analysis), Perm': Izd. Perm. Gos. SKhA, 2003, p. 140.
4. Racheva, N.L. and Maslivets, A.N., *Zh. Org Khim.,* 2008, vol. 44, no. 4, p. 515.
5. Racheva, N.L. and Maslivets, A.N., *Zh. Org Khim.,* 2006, vol. 42, p. 451.
6. Altomare, A., Cascarano, G., Giacovazzo, C. and Gualardi, A. *J. Appl. Cryst.,* 1993, vol. 26, p. 343.
7. Sheldrick, G.M., *Shelx 97. Programs for Crystal Structure Analysis,* University of Gottingen, Germany, 1998, p. 2332.