ISSN 1070-4280, Russian Journal of Organic Chemistry, 2010, Vol. 46, No. 7, pp. 1074–1078. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © N.G. Kozlov, K.N. Gusak, 2010, published in Zhurnal Organicheskoi Khimii, 2010, Vol. 46, No. 7, pp. 1075–1079.

Synthesis of Methyl-Substituted 1,7-Phenanthroline Derivatives by Condensation of 2-Methylquinolin-5-amine with Aromatic Aldehydes and Cyclic 1,3-Diketones

N. G. Kozlov and K. N. Gusak

Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus,
ul. Surganova 13, Minsk, 220072 Belarus
e-mail: loc@ifoch.bas-netby

Received June 26, 2009

Abstract—Previously unknown 7-aryl(hetaryl)-3-methyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-ones and their 10,10-dimethyl-substituted analogs were synthesized by three-component condensation of 2-methylquinolin-5-amine with aromatic aldehydes and cyclic β-diketones (cyclohexane-1,3-dione and dimedone) in butyl alcohol.

DOI: 10.1134/S1070428010070195

Some methyl-substituted aza- and diazaphenanthrene derivatives were found to exhibit analgesic and antiallergic properties, as well as bactericidal, breath stimulating, and antienzyme activity; they can also be used as diagnostic agents for detection of leukocytes and erythrocytes [1–4]. The presence of a methyl group therein is important; it is responsible for a broad spectrum of biological activity and a variety of chemical reactions that could lead to new strongly conjugated systems and polymeric materials having pharmacophoric fragments [5–10].

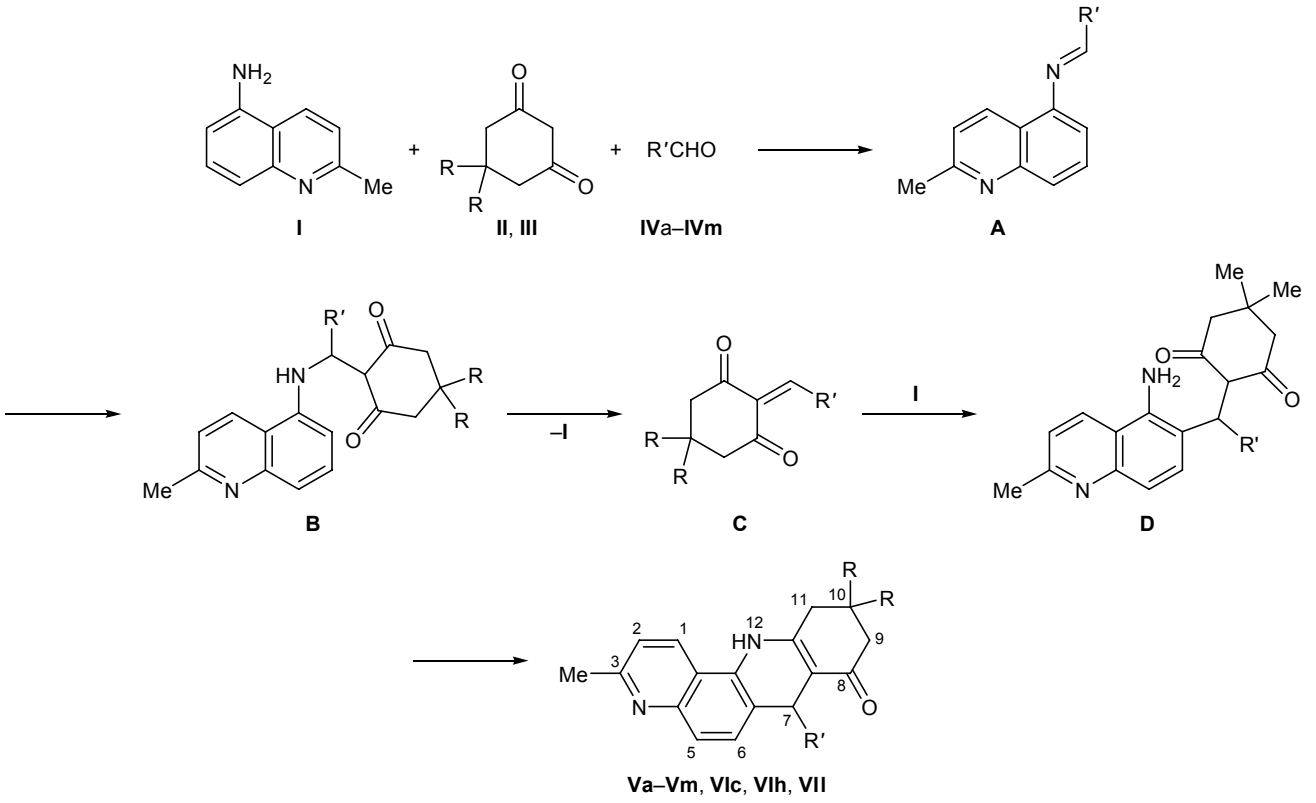
Methyl-substituted 1,7-phenanthroline derivatives have been studied poorly because of difficulties in their synthesis. Methyl-substituted nitrogen-containing heterocycles are generally obtained by condensation of aromatic amines with α,β-unsaturated carbonyl compounds, such as methyl vinyl ketone and crotonaldehyde or their precursors (acetone, formaldehyde, or paraldehyde) known as Doebner–Miller reaction. However, this reaction turned out to be weakly effective for the synthesis of 1,7-phenanthrolines from *m*-phenylenediamine or quinolin-5-amine: the yields of the target products were poor because of low reactivity of the initial amines, and the main processes were condensation and polymerization of carbonyl compounds.

We previously showed that three-component condensation of quinolin-5-amine with aromatic aldehydes and cyclohexane-1,3-dione gives fused 1,7-phenanthroline derivatives [11]. The present work was aimed at synthesizing methyl-substituted 1,7-phenanthrolines. For this purpose, we examined for the first time three-component condensation of 2-methylquinolin-5-amine (**I**) with cyclic β-diketones, cyclohexane-1,3-dione (**II**) and 5,5-dimethylcyclohexane-1,3-dione (**III**, dimedone), and aromatic (heteroaromatic) aldehydes **IVa**–**IVm**. The reactions were carried out by heating equimolar amounts of the reactants in boiling butan-1-ol. As a result, the corresponding 7-aryl(hetaryl)-3-methyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-ones **Va**–**Vm** and their 10,10-dimethyl-substituted analogs **VIc**, **VId**, and **VIl** were formed with high selectivity (yield 46–76%;).

Presumably, the formation of benzo[*b*][1,7]phenanthrolinone system involves initial condensation of amine **I** with aldehyde **IV** to give Schiff base **A**, addition of diketone **II** or **III** at the C=N bond in **A**, rearrangement of adduct **B** thus formed via elimination of α,β-unsaturated diketone **C** and its subsequent migration to the aromatic ring (to the carbon atom in the α-position with respect to the amino group, which possesses the highest electron density), and intramolecular condensation of rearrangement product **D** (Scheme 1). An alternative reaction path includes initial reaction of diketone **II** or **III** with aromatic aldehyde **IV** with formation of 2-arylmethylidenecyclohexan-1,3-dione **B** which then reacts with aminoquinoline according to the above scheme.

The substituent R′ in the aldehyde molecule somewhat affects the yield of target products **V** and **VI**. Benzaldehydes **IVa**–**IVd** and **IVl** having halogen

Scheme 1.



II, **V**, R = H; **III**, **VI**, R = Me; **IV**–**VI**, R′ = 4-FC_6H_4 (**a**), 4-BrC_6H_4 (**b**), 4-HOC_6H_4 (**c**), 3,4-$(HO)_2C_6H_3$ (**d**), 2-$MeOC_6H_4$ (**e**), 4-$MeOC_6H_4$ (**f**), 2,4-$(MeO)_2C_6H_3$ (**g**), 3,4-$(MeO)_2C_6H_3$ (**h**), 3-MeO-4-HOC_6H_3 (**i**), 4-$Me_2NC_6H_4$ (**j**), 4-$(ClCH_2CH_2)_2NC_6H_4$ (**k**), 4-$MeOCOC_6H_4$ (**l**), pyridin-3-yl (**m**).

atoms or alkoxycarbonyl or hydroxy groups in the aromatic ring, which activate the carbonyl group due to negative inductive effect, ensure fairly high yields (68–76%) of the products. Likewise, phenanthroline **Vm** was obtained in 61% yield from pyridine-3-carbaldehyde (**IVm**) where the reactivity of the aldehyde group is enhanced due to *–I* effect of the pyridine nitrogen atom. Dialkylamino-substituted phenanthrolines **Vj** and **Vk** were formed in lower yields (46–48%). The presence of methyl groups in the molecule of diketone **III** almost did not affect the yield of methylphenanthrolines.

The structure of compounds **Va**–**Vm**, **VIc**, **VId**, and **VII** was determined on the basis of their IR, NMR, and mass spectra. Their IR spectra contained strong absorption bands at 1590 and 1525 cm^{-1} due to vibrations of the vinylogous amide fragment (1580, 1520 cm^{-1} [11]). Strong bands at 3440 and 1620 cm^{-1} were assigned, respectively, to stretching and bending vibrations of the secondary amino group. Stretching vibrations of aliphatic and cycloaliphatic C–H bonds gave rise to absorption in the region 2960–2870 cm^{-1}, and stretching vibration bands of aromatic C–H bonds appeared at 3060–3030 cm^{-1}. Compounds **Ve**–**Vi**, **Vl**, and **VII** also displayed in the IR spectra absorption bands in the region 1240–1230 cm^{-1} due to vibrations of the C–O–C fragment, and ester carbonyl group in phenanthrolines **Vl** and **VII** was characterized by absorption at 1725–1720 cm^{-1}.

In the mass spectra of benzophenanthrolinones **Va**–**Vm**, **VIc**, **VId**, and **VII** the molecular ion peaks $[M]^+$ had a relative intensity of 15–43%, while the base peak (100%) was that of the $[M - R]^+$ ion: *m*/*z* 263 (**Va**–**Vm**), 291 (**VIc**, **VId**, **VII**). The spectra of all phenanthrolines contained a fragment ion peak with *m*/*z* 207 (I_{rel} 10–23%), which corresponds to elimination of CH_2CH_2CO (**Va**–**Vm**) or Me_2CCH_2CO moiety (**VIc**, **VId**, **VII**) from the molecular ion.

The ^1H NMR spectra of compounds **V** and **VI** were similar to those reported previously for structurally related 1,7-phenanthrolines having no methyl group on C^3 [11]; signals of the latter were assigned by analysis of two-dimensional COSY, NOESY, HSQC, and HMBC spectra [11]. The ^1H NMR spectra of **Va**–**Vm**,

VIc, **VId**, and **VIl** lacked signal assignable to proton on C^3, but a singlet at δ 2.58–2.67 ppm appeared due to 3-Me group. The 7-H proton in the dihydropyridine fragment resonated as a singlet at δ 5.11–5.68 ppm. It is displaced downfield [12] due to magnetically anisotropic effect of the neighboring aromatic ring. Aromatic protons in the R′ substituent suffer from deshielding effect of substituents in the phenyl ring, and the position and multiplicity of their signals are consistent with their arrangement with respect to the substituent. Methyl groups on C^{10} in dimedone derivatives **VIc**, **VId**, and **VIl** give rise to two singlets in the region δ 0.90–1.11 ppm.

Thus three-component condensation of 2-methylquinolin-5-amine with aromatic aldehydes and cyclic β-diketones provides a convenient one-pot procedure for the synthesis of a number of difficultly accessible methyl-substituted 1,7-phenanthroline derivatives. The condensation products obtained from dimedone possess a CMe_2 fragment which is typical of many biologically active compounds. However, the most promising in the structure of the obtained 1,7-phenanthrolines is the presence of a methyl group in the quinoline fragment; broad synthetic potential of that group attracts interest from the viewpoint of the design of new compounds with practically useful properties.

EXPERIMENTAL

The IR spectra were recorded in KBr on a Nicolet Protégé-460 spectrometer with Fourier transform. The NMR spectra were measured on Bruker AC-500 (500 MHz) and Tesla BS-567 (100 MHz) spectrometers from solutions in DMSO-d_6 using tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT INCOS-50 instrument, as well as on a Hewlett–Packard 5890/5972 GC–MS system (electron impact, 70 eV; HP-5MS column, 30 m×0.25 mm, film thickness 0.25 μm; injector temperature 250°C). The melting points were determined on a Kofler hot stage.

7-Aryl(hetaryl)-3-methyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-ones Va–Vm and 7-aryl-3,10,10-trimethyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-ones VIc, VId, and VIl (*general procedure*). A solution of 2-methylquinolin-5-amine (**I**), 5 mmol of cyclohexane-1,3-dione (**II**, in the synthesis of compounds **Va**–**Vm**) or 5,5-dimethylcyclohexane-1,3-dione (**III**, in the synthesis of **VIc**, **VId**, and **VIl**), and 5 mmol of aldehyde **IVa**–**IVm** in 20 ml of butan-1-ol was heated for 3–4 h under reflux. The precipitate was filtered off, washed with diethyl ether, and recrystallized from ethanol (**Va**, **Vi**), 1:3 ethanol–benzene mixture (**Vb**, **Vc**, **Vf**–**Vh**, **Vj**–**Vm**, **VIc**, **VId**, **VIl**), or dimethylformamide (**Vd**, **Ve**).

12-(4-Fluorophenyl)-3-methyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Va). Yield 75%, mp 187–188°C. ^{1}H NMR spectrum, δ, ppm: 1.93 m (1H, 10-H_{ax}), 2.08 m (1H, 10-H_{eq}), 2.24 m (2H, 9-H), 2.59 s (Me), 2.61 m (1H, 11-H_{ax}), 2.78 d.t (1H, 11-H_{eq}, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.6 Hz), 5.19 s (7-H), 7.11 d (2H, 2′-H, 6′-H, J = 8.5 Hz), 7.32 m (2H, 3′-H, 5′-H) 7.36 d (1H, 6-H, $J_{6,5}$ = 8.8 Hz), 7.40 d (1H, 2-H, $J_{2,1}$ = 8.4 Hz), 7.45 d (1H, 5-H, $J_{5,6}$ = 8.8 Hz), 8.80 d (1H, 1-H, $J_{1,2}$ = 8.4 Hz), 9.29 s (NH). Found, %: N 7.59. $C_{23}H_{19}FN_2O$. Calculated, %: N 7.82.

7-(4-Bromophenyl)-3-methyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vb). Yield 71%, mp 279–280°C. ^{1}H NMR spectrum, δ, ppm: 1.98 m (1H, 10-H_{ax}), 2.05 m (1H, 10-H_{eq}), 2.28 m (2H, 9-H), 2.60 s (3H, Me), 2.65 m (1H, 11-H_{ax}), 2.80 d.t (1H, 11-H_{eq}, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.5 Hz), 5.26 s (1H, 7-H), 7.18 d (2H, 2′-H, 6′-H, J = 8.4 Hz), 7.38 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.47 d (3H, 2-H, 5-H, 6-H, $J_{2,1} = J_{5,6}$ = 8.9 Hz), 8.82 d (1H, 1-H, $J_{1,2}$ = 8.9 Hz), 9.42 s (NH). Found, %: C 65.76; H 4.39; Br 18.90; N 6.53. $C_{23}H_{19}BrN_2O$. Calculated, %: C 65.87; H 4.53; Br 19.09; N 6.68.

7-(4-Hydroxyphenyl)-3-methyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vc). Yield 76%, mp 237–238°C. ^{1}H NMR spectrum, δ, ppm: 1.95 m (1H, 10-H_{ax}), 2.03 m (1H, 10-H_{eq}), 2.25 m (2H, 9-H), 2.63 s (3H, Me), 2.73 d.d.d (1H, 11-H_{ax}, ^2J = 17.0, $J_{11\text{-}ax,10\text{-}eq}$ = 4.3 Hz), 2.85 d.t (1H, 11-H_{eq}, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.3 Hz), 5.19 s (1H, 7-H), 6.38 d (2H, 2′-H, 6′-H, J = 8.1 Hz), 6.49 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.39 d (1H, 6-H, $J_{6,5}$ = 9.0 Hz), 7.42 d (1H, 2-H, $J_{2,1}$ = 8.9 Hz), 7.44 d (1H, 5-H, $J_{5,6}$ = 9.0 Hz), 8.64 s (1H, OH), 8.83 d (1H, 1-H, $J_{1,2}$ = 8.9 Hz), 9.25 s (NH). Found, %: C 77.42; H 5.50; N 7.74. $C_{23}H_{20}N_2O_2$. Calculated, %: C 77.53; H 5.62; N 7.86.

7-(3,4-Dihydroxyphenyl)-3-methyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vd). Yield 69%, mp 173–174°C. ^{1}H NMR spectrum, δ, ppm: 1.90 m (1H, 10-H_{ax}), 2.01 m (1H, 10-H_{eq}), 2.24 m (2H, 9-H), 2.61 s (3H, Me), 2.70 m (1H, 11-H_{ax}), 2.79 d.t (1H, 11-H_{eq}, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.8 Hz), 5.17 s (1H, 7-H), 6.58 d (1H, 6′-H, $J_{6',5'}$ = 8.6 Hz), 6.63 d (1H, 5′-H, $J_{5',6'}$ = 8.6 Hz), 6.70 s (1H, 2′-H), 7.47 d (1H, 2-H, $J_{2,1}$ = 8.8 Hz), 7.53 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.58 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 8.58 s

(1H, OH), 8.62 s (1H, OH), 8.86 d (1H, 1-H, $J_{1,2}$ = 8.8 Hz), 9.30 s (NH). Found, %: C 73.98; H 5.19; N 7.33. $C_{23}H_{20}N_2O_3$. Calculated, %: C 74.19; H 5.39; N 7.53.

7-(2-Methoxyphenyl)-3-methyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Ve). Yield 68%, mp 293–294°C. ^{1}H NMR spectrum, δ, ppm: 1.96 m (1H, 10-H$_{ax}$), 2.02 m (1H, 10-H$_{eq}$), 2.25 m (2H, 9-H), 2.60 s (3H, Me), 2.73 m (1H, 11-H$_{ax}$), 2.90 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.4 Hz), 3.90 s (3H, MeO), 5.68 s (1H, 7-H); 6.78 t, 6.90 d, 7.04 t, 7.09 t (4H, 3′-H, 4′-H, 5′-H, 6′-H, $J_{3',4'}$ = 8.0, $J_{4',5'} = J_{5',6'}$ = 8.5 Hz); 7.40 (1H, 2-H, $J_{2,1}$ = 8.7 Hz), 7.44 d (1H, 6-H, $J_{6,5}$ = 8.8 Hz), 7.58 d (1H, 5-H, $J_{5,6}$ = 8.8 Hz), 8.79 d (1H, 1-H, $J_{1,2}$ = 8.7 Hz), 9.31 s (NH). Found, %: C 77.67; H 5.83; N 7.35. $C_{24}H_{22}N_2O_2$. Calculated, %: C 77.84; H 5.94; N 7.57.

7-(4-Methoxyphenyl)-3-methyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vf). Yield 70%, mp 271–272°C. ^{1}H NMR spectrum, δ, ppm: 1.91 m (1H, 10-H$_{ax}$), 2.03 m (1H, 10-H$_{eq}$), 2.24 m (2H, 9-H), 2.60 s (3H, Me), 2.69 d.d.d (1H, 11-H$_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 17.1, $J_{11\text{-}ax,10\text{-}eq}$ = 4.3 Hz), 2.85 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.3 Hz), 3.69 s (3H, MeO), 5.22 s (1H, 7-H), 6.73 d (2H, 2′-H, 6′-H, J = 8.4 Hz), 7.13 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.48 d (1H, 2-H, $J_{2,1}$ = 8.6 Hz), 7.53 d (1H, 6-H, $J_{6,5}$ = 9.0 Hz), 7.59 d (1H, 5-H, $J_{5,6}$ = 9.0 Hz), 8.87 d (1H, 1-H, $J_{1,2}$ = 8.6 Hz), 9.39 s (NH). Found, %: C 77.55; H 5.88; N 7.27. $C_{24}H_{22}N_2O_2$. Calculated, %: C 77.84; H 5.94; N 7.57.

7-(2,4-Dimethoxyphenyl)-3-methyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vg). Yield 69%, mp 284–285°C. ^{1}H NMR spectrum, δ, ppm: 1.93 m (1H, 10-H$_{ax}$), 2.03 m (1H, 10-H$_{eq}$), 2.28 m (2H, 9-H), 2.64 s (3H, Me), 2.77 d.d.d (1H, 11-H$_{ax}$, ^2J = 17.5, $J_{11\text{-}ax,10\text{-}eq}$ = 4.4 Hz), 2.83 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.4 Hz), 3.69 s (3H, MeO), 3.75 s (3H, MeO), 5.40 s (1H, 7-H), 6.68 d (2H, 5′-H, 6′-H, $J_{5',6'}$ = 8.8 Hz), 6.81 s (1H, 3′-H), 7.43 d (1H, 2-H, $J_{2,1}$ = 8.9 Hz), 7.50 d (1H, 6-H, $J_{6,5}$ = 9.0 Hz), 7.55 d (1H, 5-H, $J_{5,6}$ = 9.0 Hz), 8.88 d (1H, 1-H, $J_{1,2}$ = 8.9 Hz), 9.36 s (NH). Found, %: C 74.73; H 5.87; N 6.90. $C_{25}H_{24}N_2O_3$. Calculated, %: C 75.00; H 6.00; N 7.00.

7-(3,4-Dimethoxyphenyl)-3-methyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vh). Yield 72%, mp 228–229°C. ^{1}H NMR spectrum, δ, ppm: 1.90 m (1H, 10-H$_{ax}$), 2.01 m (1H, 10-H$_{eq}$), 2.25 m (2H, 9-H), 2.64 s (3H, Me), 2.73 d.d.d (1H, 11-H$_{ax}$, ^2J = 17.2, $J_{11\text{-}ax,10\text{-}eq}$ = 4.5 Hz), 2.80 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.5 Hz), 3.70 s (3H, MeO), 3.77 s (3H, MeO), 5.40 s (1H, 7-H), 6.65 d (1H, 6′-H, $J_{6',5'}$ = 8.6 Hz), 6.72 d (1H, 5′-H, $J_{5',6'}$ = 8.6 Hz), 6.80 s (1H, 2′-H), 7.46 d (1H, 2-H, $J_{2,1}$ = 8.8 Hz), 7.53 d (1H, 6-H, $J_{6,5}$ = 9.0 Hz), 7.57 d (1H, 5-H, $J_{5,6}$ = 9.0 Hz), 8.81 d (1H, 1-H, $J_{1,2}$ = 8.8 Hz), 9.32 s (NH). Found, %: C 74.90; H 5.83; N 6.94. $C_{25}H_{24}N_2O_3$. Calculated, %: C 75.00; H 6.00; N 7.00.

7-(4-Hydroxy-3-methoxyphenyl)-3-methyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vi). Yield 75%, mp 220–221°C. ^{1}H NMR spectrum, δ, ppm: 1.94 m (1H, 10-H$_{ax}$), 2.03 m (1H, 10-H$_{eq}$), 2.29 m (2H, 9-H), 2.62 s (3H, Me), 2.71 d.d.d (1H, 11-H$_{ax}$, ^2J = 17.6, $J_{11\text{-}ax,10\text{-}eq}$ = 4.6 Hz), 2.80 d.t (1H, 11-H$_{eq}$, $J_{11\text{-}eq,10\text{-}ax} = J_{11\text{-}eq,10\text{-}eq}$ = 4.6 Hz), 3.72 s (3H, MeO), 5.32 s (1H, 7-H), 6.69 d (2H, 5′-H, 6′-H, $J_{5',6'}$ = 8.6 Hz), 6.80 s (1H, 2′-H), 7.47 d (1H, 2-H, $J_{2,1}$ = 8.7 Hz), 7.53 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.57 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 8.61 s (1H, OH), 8.89 d (1H, 1-H, $J_{1,2}$ = 8.7 Hz), 9.35 s (NH). Found, %: C 74.43; H 5.67; N 7.11. $C_{24}H_{22}N_2O_3$. Calculated, %: C 74.61; H 5.70; N 7.25.

7-(4-Dimethylaminophenyl)-3-methyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vj). Yield 46%, mp 187–188°C. ^{1}H NMR spectrum, δ, ppm: 1.95 m (1H, 10-H$_{ax}$), 2.03 m (1H, 10-H$_{eq}$), 2.25 m (2H, 9-H), 2.60 s (3H, Me), 2.75 m (1H, 11-H$_{ax}$), 2.82 m (1H, 11-H$_{eq}$), 3.32 s (6H, NMe$_2$), 5.11 s (1H, 7-H), 6.50 d (2H, 2′-H, 6′-H, J = 8.8 Hz), 6.97 d (2H, 3′-H, 5′-H, J = 8.8 Hz), 7.40 m (3H, 2-H, 5-H, 6-H), 8.73 d (1H, 1-H, $J_{1,2}$ = 8.9 Hz), 9.28 s (NH). Found, %: C 78.19; H 6.50; N 10.71. $C_{25}H_{25}N_3O$. Calculated, %: C 78.33; H 6.53; N 10.97.

7-[4-Bis(2-chloroethyl)]aminophenyl]-3-methyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vk). Yield 48%, mp 204–205°C. ^{1}H NMR spectrum, δ, ppm: 1.92 m (1H, 10-H$_{ax}$), 2.02 m (1H, 10-H$_{eq}$), 2.29 m (2H, 9-H), 2.58 s (3H, Me), 2.77 m (1H, 11-H$_{ax}$), 2.85 m (1H, 11-H$_{eq}$), 3.60 s [8H, N(C$_2$H$_4$Cl)$_2$], 5.16 s (1H, 7-H), 6.52 d (2H, 2′-H, 6′-H, J = 8.9 Hz), 7.03 d (2H, 3′-H, 5′-H, J = 8.9 Hz), 7.45 d (1H, 2-H, $J_{2,1}$ = 8.7 Hz), 7.52 d (1H, 6-H, $J_{6,5}$ = 9.0 Hz), 7.57 d (1H, 5-H, $J_{5,6}$ = 9.0 Hz), 8.79 d (1H, 1-H, $J_{1,2}$ = 8.7 Hz), 9.32 s (NH). Found, %: C 67.49; H 5.50; Cl 14.58; N 8.56. $C_{27}H_{27}Cl_2N_3O$. Calculated, %: C 67.50; H 5.63; Cl 14.7; N 8.75.

Methyl 4-(3-methyl-8-oxo-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-7-yl)benzoate (Vl). Yield 73%, mp 219–220°C. ^{1}H NMR spectrum, δ, ppm: 1.98 m (1H, 10-H$_{ax}$), 2.07 m (1H, 10-H$_{eq}$), 2.32 m

(2H, 9-H), 2.61 s (3H, Me), 2.73 m (1H, 11-H_{ax}), 2.84 m (1H, 11-H_{eq}), 3.79 s (3H, CO_2Me), 5.38 s (1H, 7-H), 7.32 d (2H, 2′-H, 6′-H, J = 8.7 Hz), 7.40 d (1H, 6-H, $J_{6,5}$ = 8.9 Hz), 7.46 d (1H, 2-H, $J_{2,1}$ = 8.8 Hz), 7.53 d (1H, 5-H, $J_{5,6}$ = 8.9 Hz), 7.71 d (2H, 3′-H, 5′-H, J = 8.7 Hz), 8.83 d (1H, 1-H, $J_{1,2}$ = 8.8 Hz), 9.27 s (NH). Found, %: C 75.20; H 5.45; N 6.89. $C_{25}H_{22}N_2O_3$. Calculated, %: C 75.38; H 5.5; N 7.04.

3-Methyl-7-(pyridin-3-yl)-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vm). Yield 61%, mp 168–169°C. ^{1}H NMR spectrum, δ, ppm: 1.90 m (1H, 10-H_{ax}), 2.02 m (1H, 10-H_{eq}), 2.24 m (2H, 9-H), 2.65 s (3H, Me), 2.76 m (1H, 11-H_{ax}), 2.87 m (1H, 11-H_{eq}), 5.29 s (1H, 7-H), 7.19 d (2H, 5′-H, 6′-H, $J_{5',6'} = J_{5',4'}$ = 8.6 Hz), 7.41 d (1H, 2-H, $J_{2,1}$ = 8.7 Hz), 7.49 d (1H, 6-H, $J_{6,5}$ = 9.0 Hz), 7.55 d (1H, 5-H, $J_{5,6}$ = 9.0 Hz), 8.25 d (1H, 4′-H, $J_{4',5'}$ = 8.6 Hz), 8.50 s (1H, 2′-H), 8.83 d (1H, 1-H, $J_{1,2}$ = 8.7 Hz), 9.40 s (NH). Found, %: C 77.29; H 5.50; N 12.21. $C_{22}H_{19}N_3O$. Calculated, %: C 77.42; H 5.57; N 12.32.

7-(4-Hydroxyphenyl)-3,10,10-trimethyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (VIc). Yield 72%, mp 220–221°C. ^{1}H NMR spectrum, δ, ppm: 0.90 s (3H, Me), 1.10 s (3H, Me), 2.08 d (1H, 9-H_{ax}, ^2J = 16.1 Hz), 2.22 d (1H, 9-H_{eq}, ^2J = 16.1 Hz), 2.43 d (1H, 11-H_{ax}, ^2J = 16.4 Hz), 2.55 d (1H, 11-H_{eq}, ^2J = 16.4 Hz), 2.67 s (3H, Me), 5.29 s (1H, 7-H), 6.35 d (2H, 2′-H, 6′-H, J = 8.0 Hz), 6.47 d (2H, 3′-H, 5′-H, J = 8.0 Hz), 7.40 d (1H, 6-H, $J_{6,5}$ = 9.1 Hz), 7.44 d (1H, 2-H, $J_{2,1}$ = 8.9 Hz), 7.50 d (1H, 5-H, $J_{5,6}$ = 9.1 Hz), 8.60 s (1H, OH), 8.80 d (1H, 1-H, $J_{1,2}$ = 8.9 Hz), 9.35 s (NH). Found, %: C 78.02; H 6.14; N 7.25. $C_{25}H_{24}N_2O_2$. Calculated, %: C 78.1; H 6.25; N 7.29.

7-(3,4-Dihydroxyphenyl)-3,10,10-trimethyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (VId). Yield 65%, mp 217–218°C. ^{1}H NMR spectrum, δ, ppm: 0.94 s (3H, Me), 1.11 s (3H, Me), 2.07 d (1H, 9-H_{ax}, ^2J = 16.4 Hz), 2.19 d (1H, 9-H_{eq}, ^2J = 16.4 Hz), 2.40 d (1H, 11-H_{ax}, ^2J = 16.3 Hz), 2.51 d (1H, 11-H_{eq}, ^2J = 16.3 Hz), 2.65 s (3H, Me), 5.33 s (1H, 7-H), 6.60 d (1H, 6′-H, $J_{6',5'}$ = 8.3 Hz), 6.71 d (1H, 5′-H, $J_{5',6'}$ = 8.3 Hz), 6.77 s (1H, 2′-H), 7.41 d (1H, 2-H, $J_{2,1}$ = 8.7 Hz), 7.52 d (1H, 6-H, $J_{6,5}$ = 9.0 Hz), 7.59 d (1H, 5-H, $J_{5,6}$ = 9.0 Hz), 8.60 s (1H, OH), 8.65 s (1H, OH), 8.84 d (1H, 1-H, $J_{1,2}$ = 8.7 Hz), 9.38 s (NH). Found, %: C 74.83; H 5.90; N 6.77. $C_{25}H_{24}N_2O_3$. Calculated, %: C 75.00; H 6.00; N 7.00.

Methyl 4-(3,10,10-trimethyl-8-oxo-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-7-yl)-benzoate (VIm). Yield 74%, mp 204–205°C. ^{1}H NMR spectrum, δ, ppm: 0.93 s (3H, Me), 1.09 s (3H, Me), 2.10 d (1H, 9-H_{ax}, ^2J = 16.0 Hz), 2.21 d (1H, 9-H_{eq}, ^2J = 16.0 Hz), 2.42 d (1H, 11-H_{ax}, ^2J = 16.2 Hz), 2.50 d (1H, 11-H_{eq}, ^2J = 16.2 Hz), 2.61 s (3H, Me), 3.84 s (3H, CO_2Me), 5.43 s (1H, 7-H), 7.34 d (2H, 2′-H, 6′-H, J = 8.9 Hz), 7.43 d (1H, 6-H, $J_{6,5}$ = 9.1 Hz), 7.47 d (1H, 2-H, $J_{2,1}$ = 8.8 Hz), 7.52 d (1H, 5-H, $J_{5,6}$ = 9.1 Hz), 7.79 d (2H, 3′-H, 5′-H, J = 8.9 Hz), 8.86 d (1H, 1-H, $J_{1,2}$ = 8.8 Hz), 9.29 s (NH). Found, %: C 75.93; H 5.98; N 6.53. $C_{27}H_{26}N_2O_3$. Calculated, %: C 76.06; H 6.10; N 6.57.

This study was performed under financial support by the Byelorussian Republican Foundation for Basic Research (project no. Kh07-007).

REFERENCES

1. Swiss Patent no. 290515, 1953; *Chem. Abstr*., 1955, vol. 49, p. 7606g.
2. Swiss Patent no. 296573, 1954; *Chem. Abstr*., 1956, vol. 50, p. 5040a.
3. Rittersdorf, W., Rey, H., Guethlein, W., and Rieckmann, P., FRG Patent no. 2235152, 1974; *Chem. Abstr*., 1974, vol. 80, no. 142769d.
4. Berger, D., Fey, G., Kuhr, M., and Werner, W., EPV Patent no. 14929, 1980; *Chem. Abstr*., 1981, vol. 94, no. 43719z.
5. Jastzebska-Glapa, M., Mlochowski, J., and Sliwa, W., *J. Prakt. Chem*., 1977, vol. 319, p. 883.
6. Konyukhov, V.N., P'yankova, L.N., and Pushkareva, Z.V., *Zh. Obshch. Khim*., 1962, vol. 32, p. 2745.
7. El'tsov, A.V., Nekrasov, S.V., and Smirnov, E.V., *Zh. Org. Khim*., 1972, vol. 8, p. 1309.
8. Mikhailenko, F.A. and Boguslavskaya, A.P., *Ukr. Khim. Zh*., 1971, vol. 37, p. 1031.
9. Bachowska, B. and Matusiak, G., *Khim. Geterotsikl. Soedin*., 2009, p. 95.
10. Carr, B. and Franklin, M., *J. Biochem. Mol. Toxicol*., 1999, vol. 13, p. 77.
11. Kozlov, N.G., Tereshko, A.B., and Gusak, K.N., *Russ. J. Org. Chem*., 2007, vol. 43, p. 1371.
12. Dyer, J.R., *Applications of Absorption Spectroscopy of Organic Compounds*, Englewood Cliffs: Prentice–Hall, 1965. Translated under the title *Prilozheniya absorbtsionnoi spektroskopii organicheskikh soedinenii*, Moscow: Khimiya, 1970, p. 44.