ISSN 1070-4280, Russian Journal of Organic Chemistry, 2016, Vol. 52, No. 11, pp. 1610–1615. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © M.G. Abramyants, D.A. Lomov, T.I. Zavyazkina, 2016, published in Zhurnal Organicheskoi Khimii, 2016, Vol. 52, No. 11, pp. 1617–1621.

Dehydrogenation of 1-Aryl(hetaryl)-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylic Acids and Their Esters with Dimethyl Sulfoxide

M. G. Abramyants, D. A. Lomov,* and T. I. Zavyazkina

Litvinenko Institute of Physical Organic and Coal Chemistry, ul. R. Luxembourg 70, Donetsk, 83114 Ukraine
**e-mail: lomov_dmitrii@mail.ru*

Received June 28, 2016

Abstract—Oxidative dehydrogenation of 1-aryl(hetaryl)-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylic acids derivatives with dimethyl sulfoxide leads to the formation of 1-aryl(hetaryl)-9*H*-β-carbolines. Simultaneously with the dehydrogenation decarboxylation occurs. At the oxidation with dimethyl sulfoxide of methyl 1-aryl (hetaryl)-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylicates methyl 1-aryl(hetaryl)-9*H*-β-carboline-3-carboxylates formed whose hydrolysis afforded the corresponding 1-aryl(hetaryl)-9*H*-β-carboline-3-carboxylic acids.

DOI: 10.1134/S1070428016110117

The oxidative properties of dimethyl sulfoxide are known for a long time. They were discovered for the first time at the oxidation of secondary alcohols to ketones (Pfitzner–Moffatt oxidation) [1]. Later it has been shown that this reaction can proceed in the presence of oxalyl chloride (Swern oxidation) [2]. Subsequently the limits of the oxidative opportunities of DMSO were considerably extended. It oxidizes mercaptans to disulfides [3], isonitriles to the corresponding isocyanates [4]. An oxidative amidation using DMSO of α-ketoaldehydes with dialkylamines was described [5]. Analogous reaction occurs as well in the series of acetophenone derivatives [6]. All these conversions occur selectively, and this is very important in the presence of substituents sensitive to the oxidation with the other reagents. This shows that DMSO is simultaneously a mild and selective oxidizer whose preparative possibilities call for further investigation.

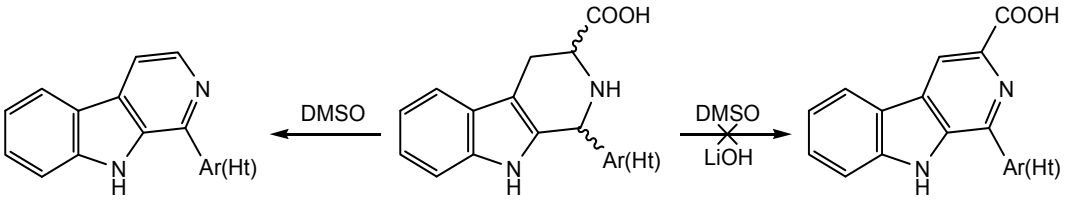
We found for the first time that DMSO is capable of oxidizing heteroaromatic structures [7]. The heating in DMSO of 4-aryl(hetaryl) spinacines in 8–10 h led to the formation of 4-aryl(hetaryl)imidazo[4,5-*c*]pyridines, in the presence of 1 equiv of LiOH they converted in 4-aryl(hetaryl)imidazo[4,5-*c*]pyridine-6-carboxylic acids. These processes are characterized by a preparative simplicity and good yields [7].

In continuation of the study of oxidative aromatization of saturated heterocyclic systems under treatment with DMSO we selected as objects of the study 1-aryl(hetaryl)-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylic acids **1a–1f**. The synthesis of compounds **1a–1d** and **1f** was described in [8], their stereochemistry (*cis*- and *trans*-isomerism) were examined in [8, 9]. In many instances the isomers were isolated and characterized. In the ^{1}H NMR spectra of isomers chemical shifts of some protons are different [8, 10].

Compound **1e** we synthesized by Pictet–Spengler reaction from tryptophan and pyridine-2-carbaldehyde. In this case also a mixture of *cis*- and *trans*-isomers was obtained that without separation was used in subsequent transformations. The ^{1}H NMR spectrum of compound **1e** alongside the signals of aromatic protons contained the proton signals of tetrahydropyridine ring of its two isomers: multiplets at 2.92 and 3.14 ppm (C^4H_2), a quartet at 3.75 ppm (H^3), and a singlet at 5.22 ppm (H^1).

At heating 1-aryl(hetaryl)-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylic acids **1a–1f** in DMSO at 90–95°C for 3–5 h they suffered dehydrogenation and decarboxylation to afford 1-aryl-(hetaryl)-9*H*-β-carbolines **2a–2f** in 58–81% yields (Scheme 1). In the ^{1}H NMR spectra of compounds **2a–2f** (as compared with the spectra of compounds **1a–1f**) the signals of

Scheme 1.



Ar(Ht) = Ph (**a**), 3-NO_2Ph (**b**), 4-NO_2Ph (**c**), 2-OHPh (**d**), 2-Py (**e**), 3-Py (**f**).

the protons of the tetrahydropyridine fragment at 2.77–5.91 ppm disappeared, and signals appeared of the vicinal protons of the pyridine fragment in the region 8.42–8.81 and 8.20–8.75 ppm.

Unlike 4-aryl(hetaryl) spinacines [7], the heating of lithium salts of compounds **1a–1f** obtained *in situ* in analogous conditions does not result in 1-aryl(hetaryl)-9*H*-β-carboline-3-carboxylic acids **5a–5f**. Instead we obtained the products of oxidative dehydrogenation and decarboxylation, compounds **2a–2f**. This may be due to the fact that compounds **1a–1f** are weaker acids than 4-aryl(hetaryl) spinacines [11], and consequently anions of compounds **1a–1f** are less stable in solution.

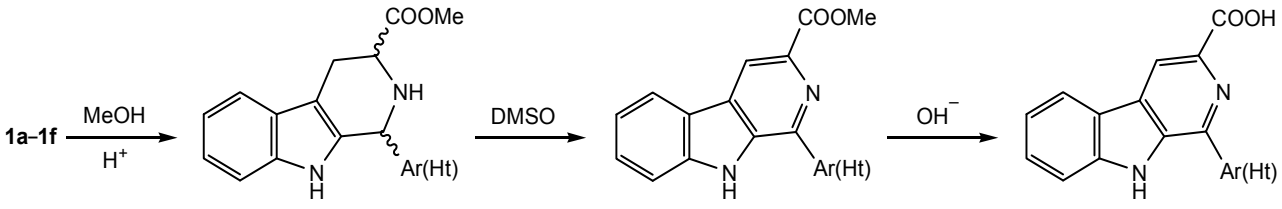
In order to prepare aromatic carboxylic acids **5a–5f** we synthesized methyl esters of acids **1a–1f**. The heating of compounds **1a–1f** in methanol in the presence of conc. H_2SO_4 at 70°C for 4–5 h led to the formation of methyl 1-aryl(hetaryl)-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylates **3a–3f** in 62–83% yield [12] (Scheme 2). Compounds **3a–3f** unlike **1a–1f** are readily soluble in chloroform, and it was utilized for their purification. The obtained esters were isolated as a mixture of two isomers that was used in further transformations without separation.

In the ^{1}H NMR spectra of esters **3a–3f** as compared to the spectra of initial acids **1a–1f** along with the proton signals of the tetrahydropyridine fragment of *cis*- and *trans*-isomers signals appeared of the protons of the methoxycarbonyl group each as three-proton singlet at 3.73–3.81 and 3.83–3.88 ppm. In the downfield region of the ^{1}H NMR spectra of some esters **3a–3f** overlapping occurs of the multiplets of the aromatic protons of two isomers, whose integral intensity corresponds to the aromatic protons in the structure of obtained esters.

The oxidation of esters **3a–3f** was performed by heating in DMSO at 90–95°C over 7–10 h. Compounds **4a–4f** were obtained in 40–81% yields. In the ^{1}H NMR spectra of methyl 1-aryl(hetaryl)-9*H*-β-carboline-3-carboxylates **4a–4f** the signals of the protons of the tetrahydropyridine fragment disappeared, and a singlet appeared from the proton in the position *4* of the pyridine fragment in the region 8.90–9.44 ppm. The doubling of the methoxycarbonyl singlet also disappears, and it shifts downfield (3.97–4.11 ppm) confirming as well the formation of esters of aromatic carboxylic acids **4a–4f**.

Hydrolysis of compounds **4a–4f** was carried out in water-alcoholic solution of alkali by heating for 3–4 h [13]. On distilling off the alcohol and acidifying the residue with 6 N HCl to pH 4–5 we isolated carboxylic acids **5a–5f** in 52–86% yields. In their ^{1}H NMR spectra the proton signal from the methoxycarbonyl group disappeared.

Scheme 2.



Ar(Ht) = Ph (**a**), 3-NO_2Ph (**b**), 4-NO_2Ph (**c**), 2-OHPh (**d**), 2-Py (**e**), 3-Py (**f**).

Hence, DMSO oxidized 1-aryl(hetaryl)-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylic acids **1a–1f** to the corresponding 1-aryl(hetaryl)-9*H*-β-carbolines **2a–2f**. Methyl esters of 1-aryl-(hetaryl)-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylic acids **3a–3f** were oxidized by DMSO to methyl esters of 1-aryl(hetaryl)-9*H*-β-carboline-3-carboxylic acids **4a–4f**.

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Bruker Avance II 400 at operating frequency 400 MHz, internal reference TMS. The homogeneity of synthesized compounds was checked by TLC on Silufol UV-254 plates, (eluent a mixture methanol–chloroform, 1 : 10, development in iodine vapor or under UV radiation).

1-(Pyridin-2-yl)-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylic acid (1e). A mixture of 2.04 g (1 mmol) of L-tryptophan, 1.18 g (1.1 mmol) of pyridine-2-carbaldehyde, 10 mL of 1 N sulfuric acid, 30 mL of water, and 5 mL of ethanol was boiled at stirring for 10 h. The separated precipitate was filtered off, washed with ethanol, dried, and recrystallized from aqueous ethanol. The reaction product was a mixture of two spatial isomers A and B. Yield 73%, mp 236–238°C (decomp.).

Isomer A. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.92 m (2H, C^{4}H$_2$), 3.75 q (1H, H^3), 5.22 s (1H, H^1), 6.94 d (1H, H^5, *J* 4.0 Hz), 7.25 d (1H, H^8, *J* 4.0 Hz), 7.43 m (2H, H^6, H^7), 7.54 d (1H, H$^{1'}$, *J* 8.0 Hz), 7.68 t (1H, H$^{3'}$), 7.79 t (1H, H$^{2'}$), 7.94 d (1H, H$^{4'}$, *J* 8.0 Hz), 10.22 s (1H, N^{9}H).

Isomer B. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.14 m (2H, C^{4}H$_2$), 3.75 q (1H, H^3), 5.22 s (1H, H^1), 7.01 d (1H, H^5, *J* 4.0 Hz), 7.27 d (1H, H^8, *J* 4.0 Hz), 7.41 m (2H, H^6, H^7), 7.58 d (1H, H$^{1'}$, *J* 8.0 Hz), 7.85 m (2H, H$^{2',3'}$), 8.02 d (1H, H$^{4'}$, *J* 8.0 Hz), 10.66 s (1H, N^{9}H). Found, %: C 69.57; H 5.17; N 14.30. $C_{17}H_{15}N_3O_2$. Calculated, %: C 69.61; H 5.15; N14.33.

Compounds 2a–2f. In 5–7 mL of DMSO was dissolved 1 mmol of 1-aryl(hetaryl)-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylic acid **1a–1f**, and the solution was heated at 90–95°C for 3–5 h. Excess DMSO was distilled off in a vacuum, the residue was recrystallized from aqueous ethanol.

1-Phenyl-9*H*-β-carboline (2a). Yield 60%, mp 215–217°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.35 t (1H, H^6), 7.55 m (2H, H^7, H$^{1'}$), 7.62 m (3H, H$^{2',4',5'}$), 7.98 m (3H, H^5, H^8, H$^{3'}$), 8.20 d (1H, H^4, *J* 8.0 Hz), 8.61 d (1H, H^3, *J* 4.0 Hz). Found, %: C 83.51; H 4.99; N 11.43. $C_{17}H_{12}N_2$. Calculated, %: C 83.58; H 4.95; N 11.47.

1-(3-Nitrophenyl)-9*H*-β-carboline (2b). Yield 58%, mp 173–175°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.38 t (1H, H^6), 7.70 m (2H, H^5, H$^{4'}$), 7.98 t (1H, H^7), 8.43 d (1H, H^8, *J* 8.0 Hz), 8.46 m (2H, H$^{2',3'}$), 8.52 d (1H, H^4, *J* 8.0 Hz), 8.61 d (1H, H^3, *J* 4.0 Hz), 8.83 s (1H, H$^{1'}$), 12.20 s (1H, NH). Found, %: C 70.51; H 3.89; N 14.44. $C_{17}H_{11}N_3O_2$. Calculated, %: C 70.58; H 3.83; N 14.53.

1-(4-Nitrophenyl)-9*H*-β-carboline (2c). Yield 81%, mp 180–182°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.38 t (1H, H^6), 7.60 m (2H, H^5, H^7), 8.04 d (1H, H^8, *J* 4.0 Hz), 8.20 d (2H, H$^{1',5'}$, *J* 8.0 Hz), 8.23 d (1H, H^4, *J* 8.0 Hz), 8.45 d (2H, H$^{2',4'}$, *J* 8.0 Hz), 8.63 d (1H, H^3, *J* 4.0 Hz). Found, %: C 70.53; H 3.88; N 14.46. $C_{17}H_{11}N_3O_2$. Calculated, %: C 70.58; H 3.83; N 14.53.

2-(9*H*-β-carbolin-1-yl)phenol (2d). Yield 71%, mp 200–202°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.05 m (2H, H$^{4',5'}$), 7.30 t (1H, H$^{3'}$), 7.37 t (1H, H^6), 7.59 t (1H, H^7), 7.72 d (1H, H^5, *J* 8.0 Hz), 8.06 d (1H, H^8, *J* 8.0 Hz), 8.22 d (1H, H$^{2'}$, *J* 8.0 Hz), 8.31 d (1H, H^4, *J* 8.0 Hz), 8.42 d (1H, H^3, *J* 4.0 Hz), 11.62 s (1H, NH). Found, %: C 78.40; H 4.68; N 10.71. $C_{17}H_{12}N_2O$. Calculated, %: C 78.44; H 4.65; N 10.76.

1-(Pyridin-2-yl)-9*H*-β-carboline (2e). Yield 71%, mp 173–175°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.31 t (1H, H^6), 7.35 t (1H, H^7), 7.59 t (1H, H$^{3'}$), 7.65 d (1H, H^5, *J* 8.0 Hz), 7.91 t (1H, H$^{4'}$), 8.01 d (1H, H^8, *J* 4.0 Hz), 8.18 d (1H, H$^{5'}$, *J* 8.0 Hz), 8.55 d (1H, H$^{2'}$, *J* 4.0 Hz), 8.75 d (1H, H^4, *J* 8.0 Hz), 8.81 d (1H, H^3, *J* 4.0 Hz), 11.39 s (1H, NH). Found, %: C 78.30; H 4.57; N 17.08. $C_{16}H_{11}N_3$. Calculated, %: C 78.35; H 4.52; N 17.13.

1-(Pyridin-3-yl)-9*H*-β-carboline (2f). Yield 71%, mp 148–150°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.35 t (1H, H^6), 7.58 m (3H, H^5, H^7, H$^{5'}$), 8.04 d (1H, H^8, *J* 8.0 Hz), 8.21 d (1H, H$^{6'}$, *J* 8.0 Hz), 8.39 d (1H, H^4, *J* 8.0 Hz), 8.62 d (1H, H$^{4'}$, *J* 4.0 Hz), 8.68 d (1H, H^3, *J* 4.0 Hz), 9.41 s (1H, H$^{2'}$), 10.01 s (1H, NH). Found, %: C 78.28; H 4.56; N 17.07. $C_{16}H_{11}N_3$. Calculated, %: C 78.35; H 4.52; N 17.13.

Compounds (3a–3f). A mixture of 1 mmol of acid **1a–1f**, 5 mmol of anhydrous methanol, and 0.2 mmol

of conc. sulfuric acid was boiled excluding moisture for 4–5 h. On distilling off methanol the residue was poured in a 5-fold volume of ice water and neutralized with a concentrated solution of sodium carbonate. The separated precipitate was filtered off, washed with water, and dried. From the dry residue the product was extracted with chloroform, chloroform was distilled off to dryness, the residue was recrystallized from methanol. Obtained esters were mixtures of two spatial isomers A and B.

Methyl 1-phenyl-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylate (3a). Yield 71%, mp 165–167°C (a mixture of isomers) {201–203°C (*cis*-isomer), 175–177°C (*trans*-isomer) [14]}.

Isomer A. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.27 m (2H, C^4H_2), 3.86 s (3H, CH_3O), 3.99 t (1H, H^3), 5.26 s (1H, H^1), 7.16–7.18 m (2H, H^5, H^6), 7.34 d (1H, H^7, *J* 4.0 Hz), 7.39 s (5H, $H^{1'-5'}$).

Isomer B. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.13 m (2H, C^4H_2), 3.73 s (3H, CH_3O), 3.99 t (1H, H^3), 5.43 s (1H, H^1), 7.16–7.18 m (2H, H^5, H^6), 7.35 d (1H, H^7, *J* 4.0 Hz), 7.48–7.62 m (5H, $H^{1'-5'}$). Found, %: C 74.45; H 5.97; N 9.10. $C_{19}H_{18}N_2O_2$. Calculated, %: C 74.49; H 5.92; N 9.14.

Methyl 1-(3-nitrophenyl)-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylate (3b). Yield 69%, mp 188–190°C (a mixture of isomers).

Isomer A. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.35 m (2H, C^4H_2), 3.85 s (3H, CH_3O), 4.02 t (1H, H^3), 5.57 s (1H, H^1), 7.15–7.20 m (2H, H^5, H^6), 7.38–7.41 m (1H, H^7), 7.49–7.59 m (3H, H^8, $H^{4',5'}$), 7.78 d (1H, $H^{3'}$, *J* 8.0 Hz), 8.31 s (1H, $H^{1'}$).

Isomer B. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.29 m (2H, C^4H_2), 3.74 s (3H, CH_3O), 4.00 t (1H, H^3), 5.42 s (1H, CH^1), 7.15–7.20 m (2H, H^5, H^6), 7.38–7.41 m (1H, H^7), 7.49–7.59 m (3H, H^8, $H^{4',5'}$), 7.68 d (1H, $H^{3'}$, *J* 8.0 Hz), 8.25 s (1H, $H^{1'}$). Found, %: C 64.90; H 4.90; N 11.90. $C_{19}H_{17}N_3O_4$. Calculated, %: C 64.95; H 4.88; N 11.96.

Methyl 1-(4-nitrophenyl)-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylate (3c). Yield 62%, mp 166–168°C (a mixture of isomers) (173–174°C [15]).

Isomer A. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.29 m (2H, C^4H_2), 3.74 s (3H, CH_3O), 3.95 t (1H, H^3), 5.56 s (1H, CH^1), 7.17–7.24 m (2H, H^6, H^7), 7.51–7.53 m (2H, H^5, H^8), 7.58 d (2H, $H^{1',5'}$, *J* 8.0 Hz), 8.20 d (2H, $H^{2',4'}$, *J* 8.0 Hz).

Isomer B. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.17 m (2H, C^4H_2), 3.85 s (3H, CH_3O), 4.02 q (1H, H^3), 5.41 s (1H, H^1), 7.17–7.24 m (2H, H^6, H^7), 7.51–7.53 m (2H, H^5, H^8), 7.63 d (2H, $H^{1',5'}$, *J* 8.0 Hz), 8.25 d (2H, $H^{2',4'}$, *J* 8.0 Hz). Found, %: C 78.31; H 4.56; N 17.10. $C_{19}H_{18}N_3O_4$. Calculated, %: C 78.35; H 4.52; N 17.13.

Methyl 1-(2-hydroxyphenyl)-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylate (3d). Yield 66%, mp 156–158°C (a mixture of isomers) {189–192°C (*cis*-isomer), 168–169°C (*trans*-isomer) [14]}.

Isomer A. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.32 m (2H, C^4H_2), 3.74 s (3H, CH_3O), 4.14 t (1H, H^3), 5.61 s (1H, H^1), 6.85–6.95 m (3H, H^6, H^7, $H^{3'}$), 7.13–7.17 m (3H, H^5, H^8, $H^{4'}$), 7.22 d (1H, $H^{5'}$, *J* 8.0 Hz), 7.53 d (1H, $H^{2'}$, *J* 8.0 Hz).

Isomer B. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.32 m (2H, C^4H_2), 3.88 s (3H, CH_3O), 3.95 t (1H, H^3), 5.38 s (1H, H^1), 6.85–6.95 m (3H, H^6, H^7, $H^{3'}$), 7.13–7.17 m (3H, H^5, H^8, $H^{4'}$), 7.22 d (1H, $H^{5'}$, *J* 8.0 Hz), 7.53 d (1H, $H^{2'}$, *J* 8.0 Hz). Found, %: C 70.75; H 5.67; N 8.64. $C_{19}H_{18}N_2O_3$. Calculated, %: C 70.79; H 5.63; N 8.69.

Methyl 1-(pyridin-2-yl)-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylate (3e). Yield 83 %, mp 154–156°C (a mixture of isomers).

Isomer A. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.49 m (2H, C^4H_2), 3.81 s (3H, CH_3O), 4.05 q (1H, H^3), 5.54 s (1H, H^1), 7.65–7.72 m (3H, H^6, H^7, $H^{3'}$), 7.92–7.94 m (2H, H^5, H^8), 8.56 d (1H, $H^{1'}$, *J* 4.0 Hz), 8.83 d (1H, $H^{4'}$, *J* 8.0 Hz).

Isomer B. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.51 m (2H, C^4H_2), 3.88 s (3H, CH_3O), 4.25 q (1H, H^3), 5.43 s (1H, H^1), 7.32–7.38 m (3H, H^6, H^7, $H^{3'}$), 7.92–7.94 m (2H, H^5, H^8), 8.04 d (1H, $H^{1'}$, *J* 8.0 Hz), 8.75 d (1H, $H^{4'}$, *J* 8.0 Hz). Found, %: C 70.30; H 5.62; N 13.65. $C_{18}H_{17}N_3O_2$. Calculated, %: C 70.34; H 5.58; N 13.67.

Methyl 1-(pyridin-3-yl)-1,2,3,4-tetrahydro-9*H*-β-carboline-3-carboxylate (3f). Yield 64%, mp 177–179°C (a mixture of isomers) {234–236°C (*cis*-isomer), 213–215°C (*trans*-isomer) [8]}.

Isomer A. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.23 m (2H, C^4H_2), 3.74 s (3H, CH_3O), 3.99 q (1H, H^3), 5.49 s (1H, H^1), 7.15–7.19 m (2H, H^6, H^7), 7.59 m (2H, H^5, H^8), 8.41– 8.52 m (3H, $H^{3'-5'}$), 8.62 s (1H, $H^{1'}$).

Isomer B. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.08 m (2H, C^4H_2), 3.85 s (3H, CH_3O), 3.99 q (1H, H^3), 5.31 s (1H, H^1), 7.15–7.19 m (2H, H^6, H^7), 7.59 m (2H, H^5, H^8), 7.72 d (1H, $H^{5'}$, *J* 8.0 Hz), 8.41–8.52 m (2H, $H^{3',4'}$), 8.55 s (1H, $H^{1'}$). Found, %: C 70.27; H 5.63; N 13.61. $C_{18}H_{17}N_3O_2$. Calculated, %: C 70.34; H 5.58; N 13.67.

Compounds 4a–4f. In 5 mL of DMSO was dissolved 1 mmol of compound **3a–3f**, and the solution was heated at 90–95°C for 7–10 h. Excess DMSO was distilled off in a vacuum, the residue was recrystallized from methanol.

Methyl 1-phenyl-9*H*-β-carboline-3-carboxylate (4a). Yield 70%, mp 250–252°C (mp 253°C [16]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.07 s (3H, CH_3O), 7.40 t (1H, H^6), 7.52 t (1H, H^7), 7.58 m (5H, $H^{1'–5'}$), 7.97 d (1H, H^5, *J* 8.0 Hz), 8.24 d (1H, H^8, *J* 8.0 Hz), 8.90 s (1H, H^4). Found, %: C 75.41; H 4.71; N 9.23. $C_{19}H_{14}N_2O_2$. Calculated, %: C 75.48; H 4.67; N 9.27.

Methyl 1-(3-nitrophenyl)-9*H*-β-carboline-3-carboxylate (4b). Yield 40%, mp 309–311°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.95 s (3H, CH_3O), 7.36 d (1H, H^5, *J* 8.0 Hz), 7.65–7.69 m (2H, H^6, H^7), 7.93 d (1H, H^8, *J* 8.0 Hz), 8.45–8.48 m (3H, $H^{3'-5'}$), 8.77 s (1H, H^4), 9.00 s (1H, $H^{1'}$), 12.14 s (1H, NH). Found, %: C 65.65; H 3.80; N 12.03. $C_{19}H_{13}N_3O_4$. Calculated, %: C 65.70; H 3.77; N 12.10.

Methyl 1-(4-nitrophenyl)-9*H*-β-carboline-3-carboxylate (4c). Yield 70%, mp 173–175°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.09 s (3H, CH_3O), 7.19 t (1H, H^6), 7.43 t (1H, H^7), 7.57 d (1H, H^5, *J* 8.0 Hz), 7.68 d (1H, H^8, *J* 4.0 Hz), 8.11 d (2H, $H^{1',4'}$, *J* 8.0 Hz), 8.25 d (2H, $H^{2',3'}$, *J* 8.0 Hz), 8.92 s (1H, H^4). Found, %: C 65.63; H 3.83; N 11.98. $C_{19}H_{13}N_3O_4$. Calculated, %: C 65.70; H 3.77; N 12.10.

Methyl 1-(2-hydroxyphenyl)-9*H*-β-carboline-3-carboxylate (4d). Yield 76%, mp 233–235°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.97 s (3H, CH_3O), 7.05–7.09 m (2H, $H^{3',4'}$), 7.36–7.44 m (2H, H^6, H^7), 7.64 d (1H, H^5, *J* 4.0 Hz), 7.75 d (1H, H^8, *J* 4.0 Hz), 8.05 d (1H, $H^{5'}$, *J* 8.0 Hz), 8.47 d (1H, $H^{2'}$, *J* 8.0 Hz), 8.98 s (1H, H^4), 12.04 s (1H, NH), 13.04 s (1H, OH). Found, %: C 71.61; H 4.47; N 8.72. $C_{19}H_{14}N_2O_3$. Calculated, %: C 71.69; H 4.43; N 8.80.

Methyl 1-(pyridin-2-yl)-9*H*-β-carboline-3-carboxylate (4e). Yield 70%, mp 181–182°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.11 s (3H, CH_3O), 7.38 t (1H, H^6), 7.60 t (1H, H^7), 7.65 d (1H, H^5, *J* 4.0 Hz), 7.92 d (1H, H^8, *J* 4.0 Hz), 8.04 d (1H, $H^{1'}$, *J* 4.0 Hz), 8.18–8.25 m (2H, $H^{2',3'}$), 8.57 d (1H, $H^{4'}$, *J* 8.0 Hz), 8.95 s (1H, H^4). Found, %: C 71.20; H 4.37; N 13.78. $C_{18}H_{13}N_3O_2$. Calculated, %: C 71.28; H 4.32; N 13.85.

Methyl 1-(pyridin-3-yl)-9*H*-β-carboline-3-carboxylate (4f). Yield 81%, mp 250–252°C (252–254°C [17]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.09 s (3H, CH_3O), 7.40 t (1H, H^6), 7.48 t (1H, H^7), 7.56–7.63 m (2H, $H^{3',4'}$), 8.26 d (1H, H^5, *J* 4.0 Hz), 8.40 d (1H, H^8, *J* 4.0 Hz), 8.56 d (1H, $H^{5'}$, *J* 4.0 Hz), 8.96 s (1H, H^4), 9.44 s (1H, $H^{1'}$), 11.47 s (1H, NH). Found, %: C 71.21; H 4.39; N 13.77. $C_{18}H_{13}N_3O_2$. Calculated, %: C 71.28; H 4.32; N 13.85.

Compounds 5a–5f. A mixture of 1 mmol of compound **4a–4f**, 5 mL of ethanol, and 2 mL of 20% water solution of KOH was boiled for 3–5 h. On removing the alcohol the residue was acidified with 6 N HCl to pH 4–5. The separated precipitate was filtered off and recrystallized from water.

1-Phenyl-9*H*-β-carboline-3-carboxylic acid (5a). Yield 58%, mp > 300°C (decomp.) {mp 283–284°C (decomp.) [15]}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.25 t (1H, H^6), 7.56 m (4H, H^7, $H^{2'–4'}$), 7.64 d (1H, H^5, *J* 8.0 Hz), 7.99 m (2H, H^8, $H^{1'}$), 8.26 d (1H, $H^{5'}$, *J* 8.0 Hz), 8.81 s (1H, H^4), 11.60 s (1H, NH). Found, %: C 74.92; H 4.27; N 9.68. $C_{18}H_{12}N_2O_2$. Calculated, %: C 74.99; H 4.20; N 9.72.

1-(3-Nitrophenyl)-9*H*-β-carboline-3-carboxylic acid (5b). Yield 53%, mp > 300°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.28 t (1H, H^6), 7.62 t (1H, H^7), 7.65 d (1H, H^5, *J* 4.0 Hz), 7.89 m (2H, H^8, $H^{5'}$), 8.33 t (1H, $H^{4'}$), 8.48 d (1H, $H^{3'}$, *J* 8.0 Hz), 8.74 s (1H, H^4), 8.83 s (1H, $H^{1'}$), 11.77 s (1H, NH). Found, %: C 64.80; H 3.39; N 12.57. $C_{18}H_{11}N_3O_4$. Calculated, %: C 64.86; H 3.33; N 12.61.

1-(4-Nitrophenyl)-9*H*-β-carboline-3-carboxylic acid (5c). Yield 52%, mp 295–297°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.36 t (1H, H^6), 7.64 t (1H, H^7), 7.71 d (1H, H^5, *J* 8.0 Hz), 8.37 d (2H, $H^{1',5'}$, *J* 8.0 Hz), 8.47 d (2H, $H^{2',4'}$, *J* 8.0 Hz), 8.49 d (1H, H^8, *J* 8.0 Hz), 9.00 s (1H, H^4), 12.14 s (1H, NH). Found, %: C 64.77; H 3.38; N 12.54. $C_{18}H_{11}N_3O_4$. Calculated, %: C 64.86; H 3.33; N 12.61.

1-(2-Hydroxyphenyl)-9*H*-β-carboline-3-carboxylic acid (5d). Yield 86%, mp 278–280°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.05–7.08 m (2H, $H^{1',2'}$), 7.32–7.41 m (2H, H^6, $H^{3'}$), 7.62 t (1H, H^7), 7.77 d (1H, H^5, *J* 8.0 Hz), 8.13 d (1H, H^8, *J* 8.0 Hz),

8.43 d (1H, $H^{4'}$, *J* 8.0 Hz), 8.94 s (1H, H^{4}), 12.05 s (1H, NH). Found, %: C 71.00; H 4.02; N 9.17. $C_{18}H_{12}N_2O_3$. Calculated, %: C 71.05; H 3.97; N 9.21.

1-(Pyridin-2-yl)-9*H*-β-carboline-3-carboxylic acid (5e). Yield 60%, mp >300°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.27 t (1H, H^{6}), 7.51 d (1H, H^{5}, *J* 8.0 Hz), 7.57 t (1H, H^{7}), 7.85 d (1H, H^{8}, *J* 8.0 Hz), 8.02 t (1H, $H^{3'}$), 8.32 d (1H, $H^{1'}$, *J* 8.0 Hz), 8.68 d (1H, $H^{4'}$, *J* 8.0 Hz), 8.85 s (1H, H^{4}), 8.87 t (1H, $H^{3'}$), 11.95 s (1H, NH). Found, %: C 70.50; H 3.85; N 14.47. $C_{17}H_{11}N_3O_2$. Calculated, %: C 70.58; H 3.83; N 14.53.

1-(Pyridin-3-yl)-9*H*-β-carboline-3-carboxylic acid (5f). Yield 63%, mp >300°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.33 t (1H, H^{6}), 7.59–7.70 m (3H, H^{5}, H^{7}, H^{8}), 8.41–8.46 m (2H, $H^{4',5'}$), 8.74 d (1H, $H^{3'}$, *J* 4.0 Hz), 8.95 s (1H, H^{4}), 9.25 s (1H, $H^{1'}$), 12.11 s (1H, NH). Found, %: C 70.49; H 3.88; N 14.42. $C_{17}H_{11}N_3O_2$. Calculated, %: C 70.58; H 3.83; N 14.53.

REFERENCES

1. Pfitzner, K.E. and Moffatt, J.G., *J. Am. Chem. Soc*., 1963, vol. 85, p. 3027.
2. Omura, K. and Swern, D., *Tetrahedron*, 1978, vol. 34, p. 1651.
3. Sanz, R., Aguado, R., Pedrosa, M.R., and Arnaiz, F.J., *Synthesis*, 2002, vol. 7, p. 856.
4. Le, H.V. and Ganem, B., *Org. Lett*., 2011, vol. 13, p. 2584.
5. Mupparapu, N., Khan, S., Battula, S., Kushwaha, M., Gupta, A.P., Ahmed, Q.N., and Vishwakarma, R.A., *Org. Lett*., 2014, vol. 16, p. 1152.
6. Wu, X., Gao, Q., Liu, S., and Wu, A., *Org. Lett*., 2014, vol. 16, p. 2888.
7. Lomov, D.A., Abramyants, M.G., Astashkina, N.V., Korotkikh, N.I., and Gres'ko, S.V., *Russ. J. Org. Chem*., 2014, vol. 50, p. 1039.
8. Ungemach, F., Soerens, D., Weber, R., DiPierro, M., Campos, O., Mokry, P., Cook, J.M., and Silverton, J.V., *J. Am. Chem. Soc*., 1980, vol. 102, p. 6976.
9. Toth, G., Szantay, J.C., Kalaus, G., Thaler, G., and Snatzke, G., *J. Chem. Soc., Perkin. Trans. 2*, 1989, p. 1849.
10. Bailey, P.D. and Hollinshead, S.P., *J. Chem. Soc. Chem. Commun*., 1985, p. 1575.
11. Braibanti, A., Dallavalle, F., Leporati, E., and Mori, G., *J. Chem. Soc., Dalton Trans*., 1973, p. 323.
12. Organikum, Moscow: Mir, 2008, vol. 2, p. 76.
13. Organikum, Moscow: Mir, 2008, vol. 2, p. 93.
14. Soerens, D., Sandrin, J., Ungemach, F., Mokry, P., Wu, G.S., Yamanaka, E., Hutchins, L., DiPierro, M., and Cook, J.M., *J. Org. Chem*., 1979, vol. 44, p. 535.
15. Snyder, H.R., Hansch, C.H., Katz, L., Parmerter, S.M., and Spaeth, E.C., *J. Am. Chem. Soc*., 1948, vol. 44, p. 219.
16. Cain, M., Weber, R.W., Guzman, F., Cook, J.M., Barker, A.S., Rice, K.C., Crawley, N.J., Paul, S.M., and Scolnick, P., *J. Med. Chem*., 1982, vol. 25, p. 1081.
17. Cain, M., Campos, O., Guzman, F., and Cook, J.M., *J. Am. Chem. Soc*., 1983, vol. 105, p. 907.