ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 4, pp. 866–870. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © L.M. Pevzner, R. Maadadi, M.L. Petrov, 2015, published in Zhurnal Obshchei Khimii, 2015, Vol. 85, No. 4, pp. 624–629.

Synthesis of Alkyl 2-Aminomethyl-5-(1,2,3-thiadiazol-4-yl)furan-3-carboxylate and Pseudopeptides on Its Basis

L. M. Pevzner, R. Maadadi, and M. L. Petrov

St. Petersburg Institute of Technology (Technical University), Moskovskii pr. 26, St. Petersburg, 190013 Russia
e-mail: pevzner _lm@list.ru

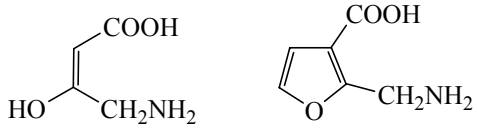
Received November 13, 2014

Abstract—Cyclization of alkyl 2-methyl-5-acetylfuran-3-carboxylate carbethoxyhydrazone according to Hurd–Mori reaction afforded alkyl 2-methyl-5-(1,2,3-thiadiazol-4-yl)-3-carboxylate. Its bromination with *N*-bromosuccinimide yielded 2-bromomethyl derivative. The latter was involved in the Delepine reaction to form alkyl 2-aminomethyl-5-(1,2,3-thiadiazol-4-yl)-3-carboxylate. Acylation of the product synthesized with chloroacetyl chloride and subsequent treatment with morpholine or 4-methylpiperidine gave the corresponding pseudopeptides. In the course of these transformations the furylthiadiazole fragment retained its stability.

Keywords: hyrazones, Hurd–Mori reaction, (1,2,3-thiadiazolyl)furans, amino acids, pseudopeptides

DOI: 10.1134/S1070363215040179

γ-Aminoacetoacetic acid and its derivatives for a long time attract the attention of neurophysiologists as the participants of metabolism of glutamate in brain, and also due to the role played by ketone bodies in the process of epilepsy [1–5]. 2-Aminomethylfuran-3-carboxylic acid is the isostere of *Z*-enol form of γ-aminoacetoacetic acid. Therefore the search of new pharmaceuticals among the compounds containing this structural fragment seems promising.

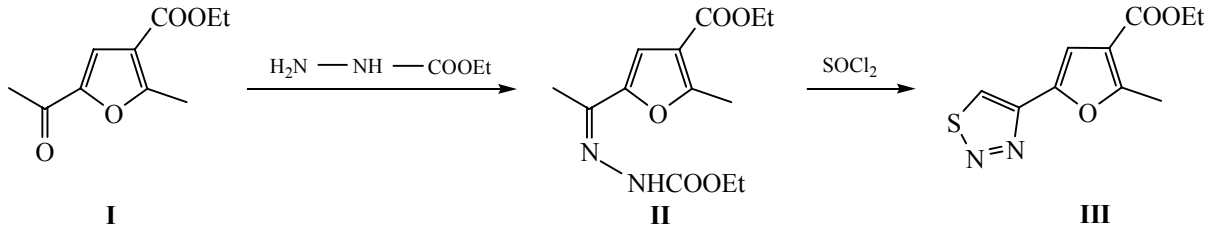


In designing enzyme inhibitors several aromatic and heteroaromatic fragments are introduced in the molecular structure for providing effective binding. Some of them are donors, and the other ones acceptors of electron density [6]. From this point of view the combination of π-deficient 1,2,3-thiadiazole with the π-excessive furan ring directly bound to one another must lead to the formation of a strongly polarized fragment.

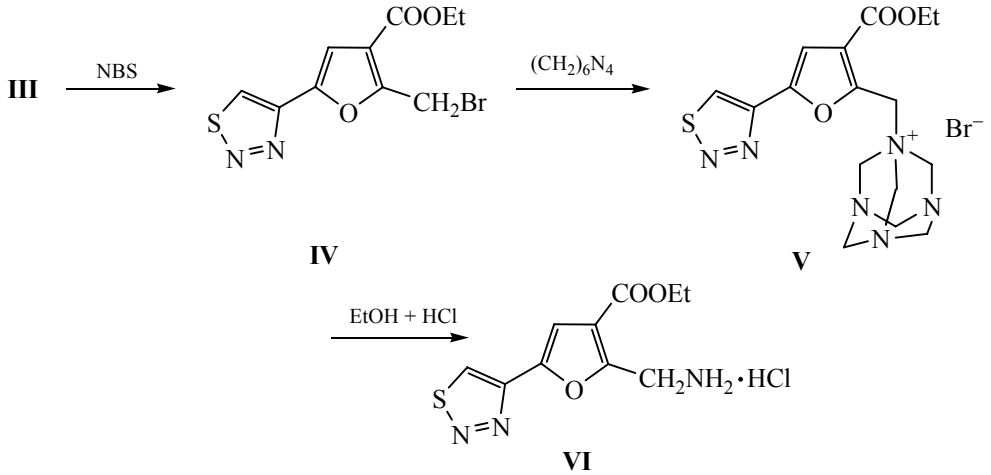
It has been shown previously [7] that 2-(1,2,3-thiadiazol-4-yl) and 3-(1,2,3-thiadiazol-4-yl)furans are thermally labile, but the introduction of electron-acceptor substituent in the position 5 of the furan ring of 2-(1,2,3-thiadiazol-4-yl)furan stabilizes this molecule and permits performing a considerably broad range of chemical transformations [8]. Considering the above-mentioned data, in this work the synthesis of the derivatives of 2-aminomethyl-5-(1,2,3-thiadiazol-4-yl)-furan-3-carboxylic acid was carried out. In the first stage it was necessary to establish whether the introduction of an ester group in the position 3 of the furan ring which is not conjugated with the thiadiazole fragment can provide the thermal stability of the system.

Easily available ethyl 2-methyl-5-acetylfuran-3-carboxylate **I** was chosen as the starting substance. It was reacted with carbethoxyhydrazine to give the corresponding hydrazone **II**. Under the action of thionyl chloride in chloroform the latter underwent cyclization according to Hurd-Mori reaction [9, 10] to form thiadiazolylfuran **III** in 87% yield. Its structure was established by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. In the ^{1}H NMR spectrum of this compound the signal of thiadiazole proton in the position 5 of the thiadiazole ring is observed at 8.58 ppm what coincides with the value of chemical shift of corresponding proton in 4-substituted 1,2,3-thiadiazoles [11]. In the mass spectrum of thiadiazole **III** an intense peak of molecular ion and the peaks of fragments arising from its decomposition with the elimination of a nitrogen molecule are observed. The isotope composition of such ions corresponds to the calculated one (Scheme 1).

Scheme 1.



Scheme 2.



Hence, the acceptor action of ester group in the position 4 of the furan ring occurs to be sufficient for the stabilization of 2-thiadiazolylfuran fragment despite of the presence of donor substituent, methyl group, in the position 5. It is interesting to mention, that all out attempts to carry out the hydrolysis of the ester **III** with the purpose of obtaining free acid failed. The latter occurred to be thermally unstable and decomposed in the course of the reaction.

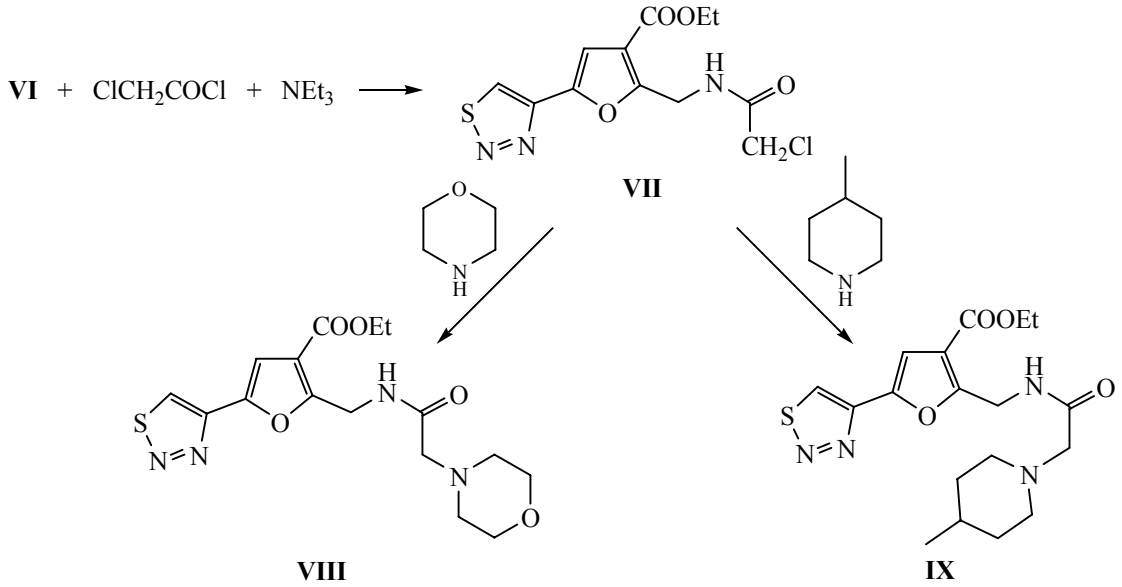
The second step of our work was the introduction of an amino group in the side chain of compound **III**. The bromination of ester **III** with *N*-bromosuccinimide in carbon tetrachloride led to the formation of bromomethyl compound **IV** in 36% yield. The substitution of bromine with amino group was carried out by Delepine reaction which was thoroughly studied for halomethyl derivatives of alkyl furoates [12] (Scheme 2).

Reaction of bromide **IV** with hexamethylenetetramine was carried out in chloroform at room temperature. Quaternary salt **V** was obtained in 61% yield. Its decomposition was carried out in ethanol solution of hydrogen chloride at the 1 : 5 molar ratio of compound **V** to HCl. Amino acid ester was isolated as hydrochloride **VI**. The admixture of ammonium chloride was removed by washing with small amount of water. In the course of isolation of free base in was found that the amino acid ester at pH 10 undergoes fast hydrolysis, and the obtained salt of amino acid quickly decomposes to form the complex mixture of water-soluble products. We failed to isolate free amino acid from it.

With the purpose of protection of potentially pharmacoforic fragment we tried to insert it in a peptide chain. Considering the lability of 5-(1,2,3-thiadiazol-4-yl)-furan-3-carboxylic acid, the modification of C-end must be carried out before the closure of the thiadiazole ring. Unlike that the *N*-end in our case is available.

The acylation of amino group was carried out with chloroacetyl chloride in methylene chloride in the presence of triethylamine at room temperature. Chloroacetamide **VII** was isolated in 63% yield. To obtain the terminal amino group it was involved in reactions with morpholine and 4-methylpiperidine. The isolation of amino esters was carried out by extraction with dilute hydrochloric acid and followed by treating with alkali until pH 8–9. Free bases **VIII, IX** occurred to be thermally stable and did not tend to hydrolysis under the isolation conditions (Scheme 3).

Scheme 3.



Hence, the introduction of an ethoxycarbonyl group in the position 4 of the furyl fragment of 4-(5-methylfur-2-yl)-1,2,3-thiadiazole provides a thermal stability to the molecule under consideration and permits carrying out the functionalization of methyl group. But when the ester and aminomethyl groups occupy neighboring positions in the furan ring the free amino ester becomes hydrolytically unstable. The increase in the distance between these functional groups by the size of a unit member of the peptide chain makes the system stable even if it contains the residue of so strong a base as 4-methylpiperidine.

We have carried out preliminary evaluation of biological activity of compounds **VIII**, **IX** with the help of PASS program [13]. It was found that both pseudopeptides with the probability ~0.7 may be anticonvulsants. Besides, compound **IX** with the probability ~0.5 may exhibit analgesic activity.

EXPERIMENTAL

Melting points were measured on the Boetius apparatus. ^{1}H and ^{13}C NMR spectra were taken on a Bruker DPX-400 spectrometer [400.13 MHz (^{1}H), 100.16 MHz (^{13}C)]. Mass spectra were obtained on a Finnigan INCOS MAT 95 spectrometer (direct admission of the sample, ionization chamber temperature 200°C, energy of ionizing electrons 70 eV). Reaction progress was controlled by TLC on Silufol UV-254 plates, development with UV light and iodine vapor.

All solvents used in this work were purified and dried according to standard protocols. Ethyl 2-methyl-3-furoate was prepared by condensation of chloroacetaldehyde with ethyl acetoacetate [14]. Acetylation of ethyl 2-methyl-3-furoate was carried out with acetic anhydride in the presence of tin tetrachloride [15].

Ethyl 2-methyl-5-acetyl-3-furoate carbethoxyhydrazone (II). To a solution of 15.5 g of ethyl 5-acetyl-3-furoate in 125 mL of 2-propanol 8.3 g of carbethoxyhydrazine and 1 mL of acetic acid were added. The reaction mixture was stirred for 8 h at 82°C. After cooling 150 mL of water was added, and the mixture obtained was left for crystallization for several hours. The obtained precipitate was filtered off and dried at room temperature. Yield 19.58 g (88%), mp 134°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.34 t (6H, CH_3-ethyl, *J* 7.2 Hz), 2.32 s (3H, CH_3-hydrazone), 2.62 s (3H, CH_3-furan), 4.28 q (2H, furan-COO$\underline{CH_2}$-CH_3, *J* 7.2 Hz), 4.30 br.q (3H, NH-COO$\underline{CH_2}$-CH_3 *J* 7.2 Hz), 6.92 s (1H, H^4-furan), 8.17 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.19 (CH_3-furan), 14.07, 14.31, 14.51 (CH_3-ethyl, CH_3-C=N), 60.35 (CH_2O-ester), 62.30 ($\underline{CH_2}$O-CONH), 111.43 (C^4-furan), 115.34 (C^3-furan), 139.81 (C^5-furan), 149.18 (C^2-furan), 154.03 (C=N), 160.67 (C=O-hydrazide), 163.53 (C=O-furan). Mass spectrum, *m/z* (I_{rel}, %): 282 (100) $[M]^+$, 237 (24), 210 (11), 194 (8), 163 (77), 135 (24), 107 (19), 93 (16), 79 (7). Found, %: C 55.14, H 6.59, N 10.05. $C_{13}H_{18}N_2O_5$. Calculated, %: C 55.31, H 6.43, N 9.92. *M* 282.29.

Ethyl 2-methyl-5-(1,2,3-thiadiazol-4-yl)furan-3-carboxylate (III). To a solution of 19.58 g of carbethoxyhydrazone **II** in 100 mL of chloroform 15.10 mL of thionyl chloride was added, and the reaction mixture was stirred for 9 h at 45–50°C. After that volatile substances were distilled off, and the residue was triturated with hexane. The obtained yellow precipitate was filtered off and dried at room temperature. Yield 14.39 g (87%), mp 80°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.38 t (3H, CH_3-ethyl, *J* 7.2 Hz), 2.69 s (3H, CH_3-furan), 4.33 q (2H, CH_2–O, *J* 7.2 Hz), 7.34 s (1H, H^4-furan), 8.58 s (1H, H^5-thiadiazole). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.88 (CH_3-furan), 14.32 (CH_3-ethyl), 60.45 (CH_2O), 110.04 (C^4-furan), 115.66 (C^3-furan), 128.75 (C^5-thiadiazole), 144.35 (C^4-thiadiazole), 153.51 (C^5-furan), 159.95 (C^2-furan), 163.50 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 238 (59) $[M]^+$, 210 (93) $[M - N_2]^+$, 181 (100) $[M - C_2H_5CO]^+$, 165 (9), 137 (18), 93 (16), 43 (38). Found, %: C 50.62, H 4.37, N 11.58. $C_{10}H_{10}N_2O_3S$. Calculated, %: C 50.41, H 4.23, N 11.76. *M* 238.26.

Ethyl 2-bromomethyl-5-(1,2,3-thiadiazol-4-yl)-furan-3-carboxylate (IV). To a solution of 2 g of thiadiazolylfuran **III** and 0.1 g of azobisisobutyronitrile in 80 mL of carbon tetrachloride 1.76 g of NBS was added. The resulting mixture was refluxed with stirring for 2.5 h until the disappearance of crystals which precipitate on the bottom of the flask after switching off the stirrer. The reaction mixture was kept for several hours at room temperature for completing the crystallization of succinimide. Then the precipitate was filtered off, the filtrate was evaporated to dryness, the residue was dissolved in methanol, and water was added in small portions until the beginning of crystallization. The mixture obtained was left for 4–5 h until the completing of crystallization, the precipitate was filtered off and dried in air. Yield 0.95 g (36%), yellow powder, mp 88°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.42 t (3H, CH_3-ethyl, *J* 7.2 Hz), 4.39 q (2H, CH_2–O, *J* 7.2 Hz), 4.91 s (2H, $BrCH_2$-furan), 7.43 s (1H, H^4-furan), 8.73 s (1H, H^5-thiadiazole). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.25 (CH_3-ethyl), 20.89 ($BrCH_2$), 61.17 (CH_2O), 110.41 (C^4-furan), 118.15 (C^3-furan), 130.20 (C^5-thiadiazole), 146.47 (C^4-thiadiazole), 153.23 (C^5-furan), 155.80 (C^2-furan), 162.23 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 318 (10) $[M + 1]^+$, 316 (9) $[M - 1]^+$, 237 (97) $[M - Br]^+$, 209 (13), 181 (100), 93 (20), 85 (27), 43 (25). Found, %: C 37.61, H 2.97, N 8.59. $C_{10}H_9BrN_2O_3S$. Calculated, %: C 37.87, H 2.86, N 8.83. *M* 317.16.

1-[3-Ethoxycarbonyl-5-(1,2,3-thiadiazol-4-yl)-2-furanylmethyl]-1-azonia-3,5,7-triazatricyclo[2.3.1.1^{3,7}]-decane bromide (V). To a solution of 0.6 g of hexamethylenetetramine in 10 mL of chloroform 1.35 g of bromide **IV** was added. The reaction mixture was stirred at room temperature until homogenization and left overnight. The obtained yellowish-grey precipitate was filtered off, washed with small amount of chloroform, and dried in air. Yield 1.19 g (61%), mp 175°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.39 t (3H, CH_3-ethyl, *J* 7.2 Hz), 4.41 q (2H, CH_2–O, *J* 7.2 Hz), 4.51 s (2H, N^+CH_2-furan), 4.57 d, 4.61 d (6H, *N*–CH_2–N, AB-system, J_{AB} 12.8 Hz), 5.33 s (6H, *N*–CH_2–N^+), 7.55 s (1H, H^4-furan), 9.65 s (1H, H^5-thiadiazole). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.63 (CH_3-ethyl), 50.51 (NCH_2-furan), 61.70 (CH_2O), 70.02 (*N*–CH_2–N^+), 78.92 (*N*–CH_2–N), 110.23 (C^4-furan), 123.65 (C^3-furan), 135.36 (C^5-thiadiazole), 146.46 (C^4-thiadiazole), 148.59 (C^2-furan), 152.40 (C^5-furan), 162.17 (C=O).

Ethyl 2-aminomethyl-5-(1,2,3-thiadiazol-4-yl)-furan-3-carboxylate hydrochloride (VI). To a solution of 2 g of hexamethylenetetraminium salt **V** in 90 mL of ethanol a solution of 0.8 g of hydrogen chloride in 2.3 mL of ethanol was added. The reaction mixture was stirred for 5 h at 78°C and then cooled to room temperature. Ammonium chloride was filtered off, and the filtrate was evaporated to dryness. The residue was suspended in 5 mL of water, the precipitate formed was filtered off and dried in air. Yield 0.8 g (63%), light yellow crystals, mp 215°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.34 t (3H, CH_3-ethyl, *J* 7.2 Hz), 4.32 q (2H, CH_2–O, *J* 7.2 Hz), 4.47 s (2H, N^+CH_2-furan), 7.44 s (1H, H^4-furan), 8.89 br.s (3H, NH_3^+), 9.57 s (1H, H^5-thiadiazole). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.55 (CH_3-ethyl), 34.89 (NCH_2-furan), 61.41 (CH_2O), 109.65 (C^4-furan), 118.59 (C^3-furan), 134.91 (C^5-thiadiazole), 146.66 (C^4-thiadiazole), 152.49 (C^5-furan), 153.67 (C^2-furan), 162.30 (C=O).

Ethyl 2-chloroacetaminomethyl-5-(1,2,3-thiadiazol-4-yl)furan-3-carboxylate (VII). To a suspension of 0.74 g of hydrochloride **VI** in 30 mL of methylene chloride 1 mL of triethylamine was added. The mixture obtained was stirred for 30 min at room temperature. After that 0.21 mL of chloroacetyl chloride was added, and the reaction mixture was stirred at room temperature for 3 h. Then it was washed with water (2 × 15 mL). The organic layer was

dried over calcium chloride and evaporated. The residue was stirred for 3 h with 5 mL of the saturated solution of sodium hydrogen carbonate, the precipitate formed was filtered off, washed with 3 mL of water, and dried in air. Yield 0.53 g (63%), mp 134°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.37 t (3H, CH_3-ethyl, *J* 7.2 Hz), 4.10 s (2H, $ClCH_2$), 4.32 q (2H, CH_2–O, *J* 7.2 Hz), 4.75 d (2H, NCH_2-furan, *J* 5.6 Hz), 7.35 s (1H, H^4-furan), 8.77 br.t (1H, NH, *J* 5.6 Hz), 9.36 s (1H, H^5-thiadiazole). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.59 (CH_3-ethyl), 35.97 (NCH_2-furan), 42.77 ($ClCH_2$), 60.90 (CH_2O), 109.79 (C^4-furan), 116.68 (C^3-furan), 133.41 (C^5-thiadiazole), 145.65 (C^4-thiadiazole), 152.80 (C^5-furan), 157.90 (C^2-furan), 162.52 (C=O-ester), 166.41 (C=O-amide).

Ethyl 2-(4-morpholinomethyl)-5-(1,2,3-thiadiazol-4-yl)furan-3-carboxylate (VIII). To a suspension of 1 g of ethyl 2-chloroacetaminomethyl-5-(1,2,3-thiadiazol-4-yl)furan-3-carboxylate **VII** in 10 mL of benzene 0.66 mL of morpholine was added, and the reaction mixture was stirred for 6 h at 80°C. After that it was extracted with the solution of 2.2 mL of concentrated hydrochloric acid in 30 mL of water. The extract obtained was drop by drop treated with ammonia until pH 8–9. The crystals formed were filtered off and dried in air at room temperature. Yield 0.34 g (29%), mp 120°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.43 br.t (3H, CH_3-ethyl, *J* 6.8 Hz), 2.56 br.s (4H, NCH_2-morpholine), 3.10 br.s (2H, $N\underline{CH_2}CO$), 3.74 (4H, CH_2O-morpholine), 4.39 br.q (2H, CH_2–O, *J* 6.8 Hz), 4.86 br.d (2H, NCH_2-фуран, *J* 5.2 Hz), 7.40 s (1H, H^4-furan), 8.10 br.s (1H, NH), 8.68 s (1H, H^5-thiadiazole). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.32 (CH_3-ethyl), 35.35 (NCH_2-furan), 53.78 (NCH_2-morpholine), 61.05 (CH_2O-ester), 61.81 ($N\underline{C}H_2CO$), 66.84 (OCH_2-morpholine), 109.90 (C^4-furan), 117.17 (C^3-furan), 129.81 (C^5-thiadiazole), 145.35 (C^4-thiadiazole), 153.41 (C^5-furan), 158.50 (C^2-furan), 163.21 (C=O-ester), 169.64 (C=O-amide).

Ethyl 2-(4-methypliperidin-1-yl)-5-(1,2,3-thiadiazol-4-yl)furan-3-carboxylate (IX). This compound was obtained analogously from 0.8 g of ethyl 2-chloroacetaminomethyl-5-(1,2,3-thiadiazol-4-yl)furan-3-carboxylate **VII** and 0.72 mL of 4-methylpiperidine. Yield 0.56 g (59%), mp 110°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.94 d (3H, CH_3-piperidine, *J* 6.4 Hz), 1.27 br.m (1H, CH^4-piperidine), 1.43 t (3H, CH_3-ethyl, *J* 7.2 Hz), 1.62 br.m (2H, CH_2^3-piperidine), 1.65 br.m (2H, CH_2^3-piperidine), 2.21 br.m (2H, NCH_2-piperidine), 2.83 br.m (2H, NCH_2-piperidine), 3.08 br.s (2H, $N\underline{CH_2}CO$), 4.39 q (2H, CH_2–O, *J* 7.2 Hz), 4.87 br.d (2H, NCH_2-furan, *J* 6.0 Hz), 7.42 s (1H, H^4-furan), 8.12 br.s (1H, NH), 8.70 s (1H, H^5-thiadiazole). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.32 (CH_3-ethyl), 21.72 (CH_3-piperidine), 30.00 (C^4-piperidine), 34.19 (C^3-piuperidine), 35.36 (NCH_2-furan), 54.27 (NCH_2-piperidine), 60.95 (CH_2O-ester), 61.69 ($N\underline{C}H_2CO$), 109.93 (C^4-furan), 117.03 (C^3-furan), 129.74 (C^5-thiadiazole), 145.39 (C^4-thiadiazole), 153.52 (C^5-furan), 158.39 (C^2-furan), 163.18 (C=O-ester), 173.89 (C=O-amide).

ACKNOWLEDGMENTS

The work was carried out with the financial support of Ministry of Education and Science of Russia within the frames of State Project.

REFERENCES

1. Yudkoff, M., Daikin, Y., Nissim, I., Grunstein, R., and Nissim, I., *J. Neurochem*., 1997, vol. 69, no. 2, p. 682. DOI: 10.1046/j.1471-4159.1997.69020682.x.
2. Daikin, Y. and Yudkoff, M., *Dev. Neurosci*., 1998, vol. 20, nos. 4–5, p. 350. DOI: 10.1159/000017331.
3. Yudkoff, M., Daikin, Y., Nissim, I., Lazarow, A., and Nissim, I., *Prostaglandin Leukot. Essent. Fatty Acids*, 2004, vol. 70, no. 3, p. 277. DOI: 10.1016/j.plefa.2003.07.005.
4. Westergaard, N., Sonnewald, U., and Schousboe, A., *Dev. Neurosci*., 1995, vol. 17, no. 4, p. 203. DOI: 10.1159/000111288.
5. McNally, M.A. and Hartman, A.L., *J. Neurochem*., 2012, vol. 121, no. 1, p. 28. DOI: 10.1111/j.1471-4159.2012.07670.x.
6. *Selleckchem.com*. Inhibitor Catalog 2014.
7. Pevzner, L.M., Remizov, Yu.O., and Petrov, M.L., *Russ. J. Gen. Chem.*, 2015, vol. 85, no. 1, p. 67. DOI: 10.1134/S1070363215010119.
8. Kuticheva, K.V., Pevzner, L.M., and Petrov, M.L., *Russ. J. Gen. Chem.*, 2015, vol. 85, no. 2, p. 424. DOI: 10.1134/S1070363215020127.
9. Raap, R. and Micetisch, R.J., *Can. J. Chem*., 1968, vol. 46, no. 7, p. 1057. DOI: 10.1139/v68-179.
10. Hurd, C.D. and Mori, R.I., *J. Am. Chem. Soc*., 1955, vol. 77, no. 20, p. 5359. DOI**:** 10.1021/ja01625a047.
11. Petrov, M.L., Kuznetsov, V.A., and Viktorov, B.N., *Russ. J. Org. Chem.*, 2010,vol 46, no. 8, p. 1214. DOI: 10.1134/S1070428010080166.
12. Lapina, I.M., Pevzner, L.M., and Potekhin, A.A., *Russ. J. Gen. Chem.*, 2006,vol 76, no. 8, p. 1304. DOI: 10.1134/S1070363206080251.
13. *www.pharmaexpert.ru/PASSOnline.*
14. Bizagni, E., Marquat, J.-P., Bourzat, J.-J., and Pepin, J.-J., *Bull. Soc. Chim. France*, 1971, p. 4041.
15. Fournier-Zaluski, M.-C. and Chatain-Cathaud, C., *Bull. Soc. Chim. France*, 1974, p. 1571.