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LETTERS TO THE EDITOR

Dedicated to the 110th anniversary of M.I. Kabachnik's birth

Reactions of Pyridoxal with Heterocycles Containing Primary Amino Group

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Abstract—New nitrogen-containing derivatives of pyridoxal were obtained as a result of its reaction with various amines. The reactions with amines bearing a heterocyclic fragment (pyridine, pyrimidine, quinoline, piperidine) furnished the final products stabilized in an aminoacetal form. The product prepared from 2-aminomethylpiperidine has an imidazolidine fragment in the molecule.

Keywords: pyridoxal, amines, azomethines, tautomerism

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In last decades extensive studies on the synthesis of functionalized derivatives of pyridoxal (vitamin B_6) and their biological activity were performed [1–3]. The pyridoxal structure includes the pyridine ring. Among the pyridine-containing compounds with biological activity the following substances should be mentioned: angioprotector Parmidinum (Prodectin), antioxidant Emoxipine, which possesses anti-hypoxic, angioprotective, antiaggregatory activity, Suprastin exhibiting anti-histamine activity, and many others [4].

Among the pyridoxal derivatives an important place is occupied by azomethines produced by its reactions with primary amines. Schiff bases originating from pyridoxal are involved into many biochemical processes such as decarboxylation, transamination, amino acids resulfation, synthesis of pyridine bases, hemoglobin and fat metabolism [5–7]. Schiff bases originating from pyridoxal contain azomethine and hydroxymethyl groups in the *ortho*-position, which predetermines their possibility to exist in both aldimine and aminoacetal forms. In the case of pyridoxal, a similar situation is observed. Sharif et al. [8] and Heinert et al. [9] consider the cyclic hemiacetal form, and in [10] the preference is given to the aldehyde form. As for pyridoxal azomethines, there are only assumptions on the possibility of stabilization of such compounds in aminoacetal form [1]. As a result of the use of a wide range of amines in the reaction with pyridoxal **1** we found examples where the final product has a non-aldimine, but aminoacetal structure (Scheme 1).

Earlier it has been illustrated by the example of α-aminopyridine [11]. In the case of its methyl derivative, 2-amino-6-picoline, an absorption band corresponding to the C=N bond (1614 cm^{-1}) is present in the IR spectrum of the solid sample. However, in the ^1H NMR spectra of a solution of the same sample there is no signal of the methine proton of the CH=N bond, and the signals at 6.80 (1H, CH, J = 6.9, 2.1 Hz) and 7.45 ppm (1H, NH, J = 6.9 Hz) are registered. The protons of the methylene group are detected as two doublets at 4.96 and 5.11 ppm with a coupling constant of 12.5 Hz, which indicates the aminoacetal form of compound **3b** in a solution.

Similar compounds **6** and **7** were obtained by reacting pyridoxal with 2-amino-4-methylpyrimidine **4** or 4-amino-2-methylquinoline **5**. These compounds can exist in two tautomeric forms: in the solid state, these are imines (C=N), and in solutions (i. e., in reactions) the aminoacetal form (CH–NH) is realized.