Thus, by modifying the structure of anabasine, it is possible to obtain substances with a higher biological activity than the alkaloid itself.

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STRUCTURE OF THE PRODUCT OF PHOTOCHEMICAL OXIDATION OF THIOCHROME

I. I. Stepuro, D. A. Oparin, V. A. Ignatenko, S. V. Zabrodskaya, T. I. Zimatkina, and G. N. Volkova

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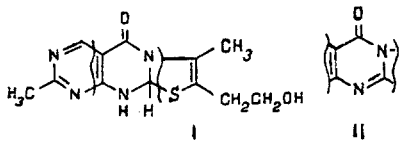
In an alkaline medium, thiamine is readily oxidized with the formation of the tricyclic compound thiochrome [1]. As is known [2], thiochrome is also formed in small amounts in the animal organism as a product of the catabolism of thiamine. On long storage, particularly in the light and in the presence of oxygen, thiochrome undergoes further transformations. We have previously [3] reported the structure of the main product of the redox disproportionation of thiochrome – oxodihydrothiochrome (I).

We have studied the photochemical oxidation of aqueous solutions of thiochrome by singlet oxygen. The reaction gave a previously unknown thiochrome transformation product (II), having a greater chromatographic mobility than thiochrome, and then oxodihydrothiochrome [R_f in the butan-1-ol–ethanol–water (2:1:1) system 0.84], $C_{12}H_{12}N_4O_2S$, M^+ 276 (mass-spectrometrically).

The singlet oxygen was generated by irradiating the dye Rose Bengal sorbed on Sephadex G-25 and present in an aqueous solution of thiochrome. Irradiation was performed with visible light, using a ZhS-17 filter. In independent experiments, singlet oxygen was obtained chemically in the reaction of bromine with H_2O_2 [4].

PMR spectrum (300 MHz, D_2O, internal standard TSP, δ, ppm): 1.96 (3H, s, CH_3-7), 2.69 (3H, s, CH_3-2), 3.18 (2H, t, J = 8 Hz, CH_2-α), 4.20 (2H, t, J = 8 Hz, CH_2-β), 8.35 (1H, s, H-4); IR spectrum ($\nu_{max}^{CHCl_3}$, cm^{-1}): 1725 (C=O), 1694 (C=N); UV spectrum ($\lambda_{max}^{H_2O}$, nm): 337 (pH 7), 355 (pH 3); fluorescence spectrum (H_2O; $\lambda_{max}^{emission}$, nm): 450 (pH 7), 475 (pH 3). From its combination of physicochemical properties, the new thiochrome transformation product was characterized as 8-(2-hydroxyethyl)-2,7-dimethyl-5-oxo-5,6-dihydrothiazolo[2,3-a]pyrimido-[4,5-d]pyrimidine (II).



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Institute of Biochemistry, Belorussian SSR Academy of Sciences, Grodno.

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Oxothiochrome (II) can also be obtained chemically. It has been shown that on the oxidation of thiochrome with Beckman's mixture or $KMnO_4$ in the presence of sodium carbonate, in spite of the temperature and time of the reaction being varied within wide limits, (II) is formed in trace amounts. When thiochrome was oxidized with $K_2Cr_2O_7$ in CH_3COOH–$(CH_3CO)_2O$ (4:1) (100°C, 1-2 h) the yield of (II) increased, amounting to 20-30%. Oxothiochrome is also formed on the oxidation of (I) by H_2O_2 or by iodine in the presence of potassium carbonate.

In experiments on mice it was shown that (II) in a dose of 10 mg/kg exhibits a weak antivitamin action, suppressing the activity of transketolase in the blood and liver by 19 and 24% (after 12 h), respectively, and that of pyruvate dehydrogenase in the liver by 31% (after 3 h).

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CHEMICAL-ENZYMATIC SYNTHESIS OF 1-(β-D-ARABINOFURANOSYL)THYMINE

A. I. Zinchenko, V. N. Barai, S. B. Bokut', E. I. Kvasyuk, and I. A. Mikhailopulo

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1-(β-D-Arabinofuranosyl)thymine (spongothymidine, aT) (V), first isolated from the Caribbean sponge Cryptotethia crypta, is of interest for the chemotherapy of oncogenic and viral diseases [1, 2]. However, a detailed study of the biological properties of aT is complicated by its poor availability for research workers, which, in its turn, is due to the absence of satisfactory methods of synthesizing this nucleoside.

In the present work we have demonstrated the possibility of a chemical-enzymatic production of aT starting from inosine (I) and thymine (III).

The phosphorolysis of inosine (I) under the action of Escherichia coli purine nucleoside phosphorylase formed hypoxanthine and α-D-ribofuranose 1-phosphate (II). The latter acted as the substrate of another reaction catalyzed by uridine phosphorylase, as a result of which compound (II) and thymine (III) formed ribothymidine (IV), isolated by chromatography on silica gel with a yield of 45% calculated on the initial thymine (III).

As a complex enzyme preparation containing both the enzymes mentioned we used whole cells of the bacterium E. coli BM-11 [3].

The interaction of the riboside (IV) with acetylsalicyloyl chloride [4] followed by precipitation of the product from the reaction mixture with ether gave the derivative 1-($O^{2'}$, 2'-anhydro-β-D-arabinofuranosyl)thymine [4], which, without isolation in the individual form, was treated with 0.5 N solution of HCl in water–dioxane (9:1). After neutralization with Dowex 1 × 8 ion-exchange resin in the OH^- form, evaporation to dryness, and crystallization of the residue from ethanol, aT was obtained with a yield of 55%. Chromatography of the residue from crystallization on a column of silica gel L 40/100 (Czechoslovakia) and elution by the $CHCl_3$–MeOH (5:1) solvent system led to the isolation of an additional amount of aT, the total yield of which was 70%.

Institute of Bioorganic Chemistry, Belorussian SSR Academy of Sciences, Minsk. Institute of Microbiology, Belorussian SSR Academy of Sciences, Minsk.

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