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).

## LITERATURE CITED


1. V. M. Berezovskii, The Chemistry of the Vitamins [in Russian], Pishchevaya Prom-st', Moscow (1973), p. 381.
2. Yu. M. Ostrovskii, Active Centers and Groupings in the Thiamine Molecule [in Russian], Nauka i Tekhnika, Moscow (1975), p. 398.
3. D. A. Oparin, I. I. Stepuro, V. I. Kondrakov, T. I. Zimatkina, V. U. Buko, F. S. Larin, and Yu. M. Ostrovskii, Khim. Prir. Soedin., 724 (1985).
4. E. McKeown and W. A. Waters, J. Chem. Soc., 1040 (1966).


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


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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%.

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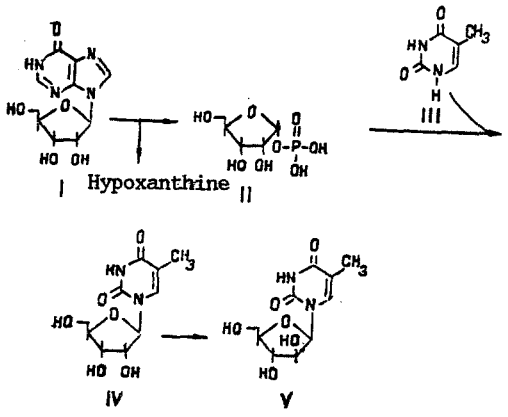


1-(β-D-Arabinofuranosyl)thymine (V): mp 246-247°C; Rf 0.73 ($CHCl_3$–MeOH (4:1); Silufol UV-254 plates). UV spectrum: $\lambda_{max}^{H_2O}$, pH 7, nm: 268 (log ε 10.3). PMR (100 MHz, DMSO): 7.5 (1H, s, H-6), 5.94 (1H, d, H-1', $J_{1',2'}$ = 4 Hz), 3.96 (2H, m, H-2', 3'), 3.63 (3H, m, H-4', 5', 5''), 1.77 (3H, s, $CH_3$).

Found, %: C 46.40; H 5.35; N 10.65. $C_{10}H_{14}N_2O_6$. Calculated, %: C 46.51; H 5.46; N 10.84 M 258.2.

LITERATURE CITED

1. G. R. Pettit and R. H. Ode, Biosynthetic Products for Cancer Chemotherapy, Plenum Press, New York (1979), Vol. 3, p. 162.
2. P. F. Torrence, Anticancer and Interferon Agents. Synthesis and Properties, Marcel Dekker, New York (1984), p. 113.
3. L. A. Eroshevskaya, V. N. Barai, A. I. Zinchenko, E. I. Kvasyuk, and I. A. Mikhailopulo, Antibiot. Med. Biotekhnol., 31, No. 3, 174 (1986).
4. A. A. Akhrem, G. V. Zaitsev, E. N. Kalinichenko, and I. A. Mikhailopulo, Bioorg. Khim. 2, No. 10, 1325 (1976).

# INFLUENCE OF THE FREE CARBOXY GROUP OF GIBBERELLIN $A_3$ ON THE RATE OF ITS ISOMERIZATION IN AQUEOUS AMMONIA

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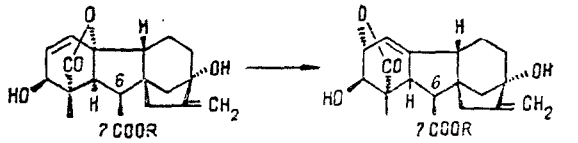
It is known that in aqueous alkaline solutions the phytohormone gibberellin $A_3$ (I) [1] and its methyl ester (II) are quantitatively converted into iso-$A_3$ (III) and the methyl ester of iso-$A_3$ (IV), respectively [2]. MacMillan et al. [3], investigating the mechanism of this reaction, assumed that the completeness of the ionization of the remote 7-carboxy group does not affect the occurrence of isomerization.




I. R=H ; II. R=$CH_3$ III. R=H ; IV. R=$CH_3$

We have made a comparative study of the isomerization of compounds (I) and (II) in 1 M aqueous ammonia at 18°C with the initial concentrations of 0.04 M for (I) and 0.009 M for (II). The disappearance of substances (I) and (II) was monitored by the HPLC method on a reversed-phase column with detection at a wavelength of 200 nm [4]. For the methyl ester of

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