

SIMPLE METHOD OF OBTAINING 1-(β -D-ARABINO-
FURANOSYL)-4-THIOURACIL AND ITS PHOSPHORIC ESTERS

L. I. Kolobushkina, A. M. Kritsyn,
S. N. Mikhailov, N. I. Spiridonova,
and V. L. Florent'ev

UDC 547.963.32'854.83.07

The amino group in cytidine derivatives is readily replaced by a thione group under the action of liquid hydrogen sulfide in aqueous pyridine solution [1, 2].

We have found that in aracytidine and its phosphoric esters, likewise, an amino group is readily replaced by sulfur under similar conditions. This method is a convenient and rapid one for obtaining 4-thioarauridine and its phosphates.

1-(β -D-Arabinofuranosyl)-4-thiouracil (4-Thioarauridine). A mixture of 243 mg (1 mmole) of aracytidine [3], 2.5 ml of water, 2.5 ml of pyridine, and 5 ml of liquid hydrogen sulfide was heated in an autoclave at 80°C for 48 h. After evaporation of the volatile substances, the reaction mixture was dissolved in the minimum volume of propanol and the nucleoside was precipitated with petroleum ether (bp 40-70 C). Yield 168 mg (65%). Found, %: C 41.5; H 4.6. $C_9H_{12}N_2O_5S$. Calculated, %: C 41.5; H 4.6. UV spectrum, λ_{max} , nm (ϵ): 0.1 N HCl 331 (19600); pH 7 331 (20400); 0.1 N KOH 311 (18600).

4-Thioarauridine 3'-Phosphate. To a solution of 125 mg (0.3 mmole) of the dihydrate of the dilithium salt of aracytidine 3'-phosphate [4] in 1 ml of water and 1 ml of pyridine was added 2 ml of liquid hydrogen sulfide and the reaction mixture was heated in an autoclave at 80°C for 18 h. After evaporation, the residue was dissolved in water, the solution was filtered, the filtrate was evaporated to small volume, and an excess of absolute ethanol was added. This gave 84 mg (70%) of the nucleotide. Found, %: C 27.9; H 3.8. $C_9H_{11}Li_2N_2O_8PS \cdot 2H_2O$. Calculated, %: C 27.8; H 3.9. UV spectrum, λ_{max} , nm (ϵ): 0.1 N HCl and at pH 7 330 (17920); 0.1 N KOH 316 (18000).

LITERATURE CITED

1. T. Ueda, M. Imawaza, K. Miura, T. Iwata, and K. Odajima, *Tetrahedron Lett.*, 2507 (1971).
2. L. I. Kolobushkina, A. M. Kritsyn, and V. L. Florent'ev, *Khim. Geterotsikl. Soedin.*, 996 (1973).
3. K. Kikugawa and M. Ichino, *J. Org. Chem.*, 37, 284 (1972).
4. J. Nagjvary, *J. Amer. Chem. Soc.*, 91, 5409 (1969).

Institute of Molecular Biology, Academy of Sciences of the USSR, Moscow. Translated from *Khimiya Geterotsiklichesikh Soedinenii*, No. 8, pp. 1143-1144, August, 1973. Original article submitted January 22, 1973.

© 1975 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.