# STRUCTURE AND REACTION OF 5-THIOFORMYLURACIL DERIVATIVES

Kosaku Hirota, Keiko Kubo, Hironao Sajiki, Yukio Kitade, Magoichi Sako, Yoshifumi Maki, Masaru Kido,* and Kazuyuki Nakagawa*

Gifu Pharmaceutical University, 5-6-1 Mitahora-higashi, Gifu 502, Japan

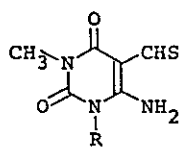
*Tokushima Research Institute, Otsuka Pharmaceutical Co., Ltd., Kagasuno, Kawauchi-cho, Tokushima 771-10, Japan

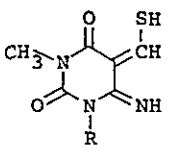
Simple thioaldehydes are unstable compounds and were until very recently known almost exclusively as cyclic trimers. On the other hand, some heterocyclic thioaldehydes stabilized by the mesomeric effect due to ring nitrogen have been synthesized, but there are few investigations on their reactivity. We describe here the structure and reactivity of 5-thioformyluracils (1) stabilized by the neighboring 6-amino-group.

6-Amino-5-thioformyluracils (1) were prepared by the reaction of 6-amino-uracils with the Vilsmeier reagent (DMF-$POCl_3$) and then NaSH according to Raid's method. These compounds have two possible structures, a thioketo form (1) and a thiol form (2). Their structures were determined to be the former (1) by X-ray diffraction analysis of (1:R=Ph).

Thioformyluracil (1a:R=Me) was treated with amines, active methylene compounds, and the Wittig reagents at room temperature to afford smoothly the corresponding condensed-products (3). In the above reaction the use of the reagents possessing a cyano group, e.g. $CH_2(CN)_2$, $CH_2(CN)COOEt$, and $Ph_3P{=}CHCN$, led to the formation of pyrido[2,3-d]pyrimidines (4: $R^1$=CN, COOEt, H; $R^2$=$NH_2$) in high yield. Treatment of (1a) with enamines caused cycloaddition to give pyrido[2,3-d]pyrimidines (4) in high yield.

Thus the thioaldehyde (1a) behaved much like aldehydes in its reactions with nucleophiles and the Wittig reagents, yielding the same products. However, (1a) underwent such reactions more readily than the corresponding 6-amino-5-formyluracil (3:X=O).


(1)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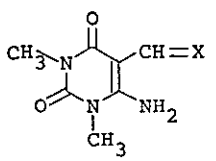
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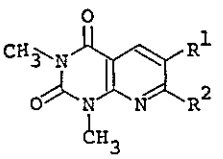
(4)