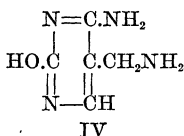
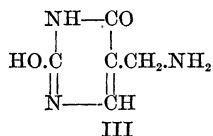


structure II for this vitamin, which differs from the Makino and Imai formulation in one respect only; in the position assigned to the methyl group substituted in the pyrimidine ring. In the Japanese formula I this group is substituted in position -4, while in formula II the methyl radical occupies position -2 of the pyrimidine cycle.

These conclusions are very important and add new interest to experimental work which has been in progress in the Yale Laboratory for several months. We are dealing here with a new and most interesting postulation, in so far as our knowledge of pyrimidine chemistry is concerned, and that is the fact that a side chain substitution characterizes the structure of the pyrimidine moiety of the vitamin molecule. We have at present very limited knowledge of the chemistry of such pyrimidine constructions, and evidence has been accumulated in pyrimidine researches already carried out in the Yale Laboratory showing that pyrimidine derivatives of this type are characterized by unique chemical properties. The study of several of these representatives of physiological interest is now in progress.

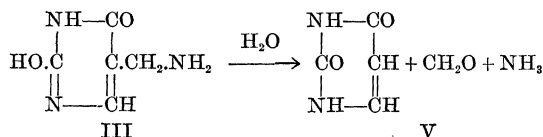
Predicating the probable physiological importance of several of these pyrimidine derivatives of the uracil type, the senior author started new work on this subject in 1934 and decided to undertake at first the development of a practical method for synthesizing the hitherto unknown amino derivative of thymine, namely, "Thyminyl-amine" III. This pyrimidine may be considered as an oxidized form of the pyrimidine cycle functioning in vitamin B₁. Its structural relationship to the proposed vitamin formulas, I or II, is clearly revealed when its constitution is expressed in its enolic form III. The corresponding 6-amino-pyrimidine expressed by formula IV is a derivative of 5-methyleytosine.



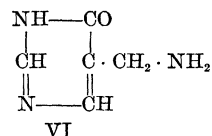
Due to a serious illness the senior author was unable to carry out his complete program of synthesis during 1935, and he turned over a part of the work to an assistant, Miss Anne Litzinger, who has accomplished successfully the synthesis of the desired thyminyl-amine III. A description of this synthesis will be presented for publication in a future number of the *Journal of the American Chemical Society*. Work dealing with the synthesis of the amino derivative of 5-methyleytosine IV is now in progress.

While the complete details of Miss Litzinger's investigation will not be reported in full until later, we do wish to make known at this time a characteristic

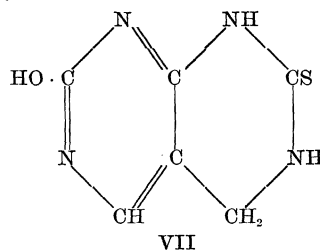
chemical behavior of thyminyl-amine III when an aqueous solution of this pyrimidine is heated. Under such conditions the amine is broken down smoothly with formation of uracil V, formaldehyde and ammonia. This hydrolytic degradation is expressed by the equation below:



In the form of its salts the pyrimidine base interacts normally as a primary amine and its derivatives crystallize well and are easily purified. The question whether a corresponding aliphatic amine of the type represented by formula VI will undergo a similar change by hydrolysis will soon be decided in this laboratory.



Starting with the methyl-cytosine derivative IV it will be possible for us to synthesize a cyclic thiourea leading to the formation of a *thiodipyrimidine*, VII. Such a construction is of immediate biochemical interest on account of its possible structural relationship to *thiochrome*.



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