

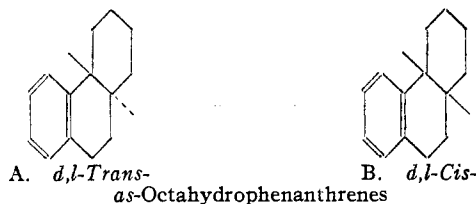
The product thus obtained, after refluxing with sodium and distilling off, was fractionated, using a Widmer fractionating column.

By repeated fractionation (until constancy of physical data was reached) the *as*-octahydrophenanthrene was separated into two main fractions, A and B, and a relatively small mixed fraction.

TABLE I

Fraction	A (20%)	B (70%)
B. p., { °C.	135.5-135.7	142.6-142.8
{ Mm.	10.5-10.8	9.2
Refr. index	n_D^{15} 1.5460	n_D^{10} 1.5592
d_4^{25}	0.9828	1.0053

From a comparison of the above data with those of *trans*- and *cis*-decahydronaphthalene [Hückel, *Ann.*, **441**, 42 (1925)], we assign by analogy to the hydrocarbon A the *trans*-configuration and to the hydrocarbon B the *cis*-configuration.



It is possible that on repeating this separation on a larger scale, we will obtain slightly different and better physical data on the isomeric *as*-octahydrophenanthrenes. Furthermore, the possibility that one of the fractions may be a constant boiling mixture, still remains. We have prepared from each of the isomers a methyl ketone, its semicarbazone, and the carboxylic acid by oxidation of the methyl ketone.

TABLE II
DERIVATIVES OF

	<i>trans</i> - AND <i>cis</i> - <i>as</i> -OCTAHYDROPHENANTHRENE	
	<i>Trans</i> -, m. p., °C.	<i>Cis</i> -, m. p., °C.
—COCH ₃	94-94.5	Oily
—semicarbazone	230-231.5	211-213
mixed m. p.	192-203	
—COOH	226-228	230-232
mixed m. p.	180-190	

We wish to mention the remote possibility that the acetyl group and consequently the carboxyl group are attached in different positions in the two hydrocarbons. Furthermore, it has to be taken into account that, in the Friedel-Crafts reaction, partial isomerization may have taken place through the action of the aluminum chloride [cf.

Zelinsky and Turowa-Pollak, *Ber.*, **65**, 1299 (1932)].

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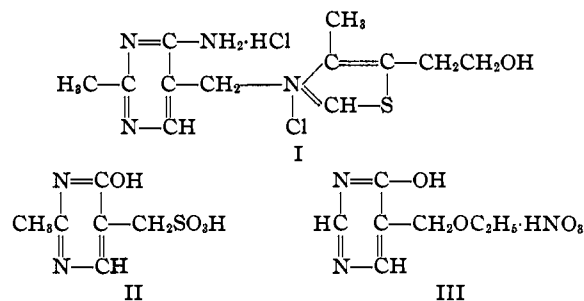
JACOB VAN DE KAMP
ERICH MOSETTIG

RECEIVED MAY 13, 1936

STRUCTURE OF VITAMIN B₁

Sir:

Certain provisional features of the structure previously proposed [THIS JOURNAL, **57**, 229 (1935)] require revision. We now feel justified in proposing Structure I for the vitamin.



We obtained by liquid ammonia cleavage of the vitamin a free base, C₆H₁₀N₄, which gives a double banded absorption quite different from the single bands of 2,6, 4,6 or 5,6-diaminopyrimidines but closely akin to those of 5-alkyl 6-amino pyrimidines. (Alkyl groups in position 5 have a profound influence on absorption of 6-amino pyrimidines; alkyls in other positions have minor effects.) The ultraviolet absorption of an extended series of pyrimidines provided convincing evidence that the second amino group of the base, C₆H₁₀N₄, is in a side chain. This base forms a dipicrate, m. p. 225°, presumably identical with the picrate of Windaus [*Z. physiol. Chem.*, **237**, 100 (1935)].

My associate, Dr. J. K. Cline, was also able to obtain from the amino sulfonic acid [THIS JOURNAL, **57**, 1093 (1935)] by the action of sodium in liquid ammonia a small yield of a base, C₆H₉N₃, which was identified by mixed melting points of the picrates, 221°, as 2,5-dimethyl-6-amino-pyrimidine which was synthesized for absorption studies. This is the first identified pyrimidine to be obtained from the vitamin. Its significance was greatly enhanced by subsequent synthesis of II which is undistinguishable by any known means from the oxy sulfonic acid of natural origin [Ref. 3].

We have synthesized five new ethoxy derivatives of 6-oxy-pyrimidine; others are described

in the literature. In general, when the ethoxy group is on a methylene group in position 2 or 4 or directly on the ring in position 5, these pyrimidines form nitrates which resemble the Windaus' oxidation product [*Z. physiol. Chem.*, **228**, 28 (1934)] $C_7H_{11}N_3O_5$, in absorption [Smakula, *ibid.*, **230**, 231 (1934)] and in solubilities. We infer that Windaus' product has the structure III but have not been able as yet to effect a synthesis for confirmation. Nitric acid is evidently not added across the double bond in positions 4-5 as in oxy-nitrothymine as such addition grossly modifies absorption.

We have long been delayed by misinterpretation of some earlier results. First, the formyl derivatives of 5,6-diaminopyrimidines exhibit absorption resembling that of the vitamin. This we now regard as fortuitous. Second, we ob-

tained crystalline formamidine (hitherto unknown) by fusing the amino sulfonic acid with sodamide. Formamidine is apparently not derived from the ring as we once supposed but probably from the methylene bridge. At another time we obtained a cleavage product with absorption indicative of a 4,6-diaminopyrimidine, the second amino group, as we now see it, being introduced by reaction rather than preëxisting in the vitamin. Following these false leads, we have attempted the synthesis of various isomers of the vitamin with considerable success but with uniformly negative physiological results and are now engaged in devising a synthesis of structure I.

Abundant activity has been obtained in such a synthetic reaction mixture.

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R. R. WILLIAMS

RECEIVED MAY 23, 1936

NEW BOOKS

Dictionary of Organic Compounds. Volume II: Ecaine-Myrtilin Chloride. Edited by I. M. HEILBRON, D.S.O., D.Sc., Ph.D., F.I.C., F.R.S., Sir Samuel Hall Professor of Chemistry, University of Manchester, and H. M. Burnbury, M.S.C., A.I.C., Imperial Chemical Industries Ltd. Oxford University Press, 114 Fifth Avenue, New York, 1936. 846 pp. Price \$30 or \$75 for the set of three volumes.

The spontaneous and flattering reception accorded the initial volume of the "Dictionary of Organic Compounds" may be construed as a verdict that Heilbron's new contribution to the classification of carbon compounds will be ranked in importance along with Beilstein and Richter. That the authors are greatly encouraged "to maintain and even enhance the standard attained" in Volume I is attested by the fact that Volume II, which has just been issued by the Oxford University Press, "although originally intended to be of approximately the same size as Volume I, actually contains nearly 150 pages more."

Several outstanding features of the English work make a strong appeal: its relatively low cost; the alphabetical classification with the obvious advantage where ready reference is concerned; the inclusion under each compound listed of all descriptive data and functional derivatives ordinarily desired; the limited number of selected literature references which means a great saving in time where unessential detail is not demanded; and, finally, a review of the literature through the year prior to the date of publication of each volume.

Before the appearance of Heilbron, abstract journals were relied on in large part to supplement Beilstein in the preparation of up-to-date bibliographies. In this connection the following announcement in the Preface of the second volume is of interest: "No addendum has been found necessary, since the literature has been completely covered up to the end of 1934. Opportunity has been taken to add as many 1935 references as the exigencies of going to press would allow."

The benefits of an authoritative lexicon like Heilbron are well exemplified by the structural relationships of recent development among the coloring pigments in plant life. Here a mass of xanthenes, flavones, flavonols and anthocyanidins have been isolated from natural sources and their complex structures established. A picture of the wonderful revelations in this important domain of organic chemistry is presented only when one can visualize the recently cleared-up substitutions and molecular rearrangements which are concerned in the metamorphosis of one product to another. What applies here is true all through Organic Chemistry; in the past few years many new fields have been explored and the accumulation of new facts has been so rapid that only the specialist in each particular domain can qualify as an authority in his realm.

Of necessity, in Heilbron, where will be crowded a vast subject matter into three volumes, will not be found thousands of known organic compounds. The only work which now embraces or probably ever will embrace an exhaustive survey is Beilstein. But here there exists at present a