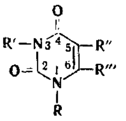
LETTERS TO THE EDITOR

DISSOCIATION CONSTANTS OF SOME URACIL DERIVATIVES

M. Draminski and B. Fiszer

In the course of our investigations in the field of alkyluracils [1], we have obtained a number of N-methylated derivatives of 5- and 5,6-alkylated uracils [2]. The dissociation constants of the compounds obtained show that the proton present at N_3 is more mobile than that at N_1.



Similar observations have been reported in the literature for uracil [3], thymine, 5-bromouracil, and the corresponding derivatives of cytosine [5]. In a paper by Stankevich et al. [6] relating, in particular, to 6-aminouracil the contrary phenomenon is reported, namely an increased mobility of the proton at N_1 as compared with that at N_3. It appears to us that this can be explained by the conjugation of the free pair of electrons on the nitrogen of the amine group with the ring, which leads to the hindered dissociation of the proton at N_3. This observation is confirmed by the dissociation constant of 5-aminouracil [7].

TABLE 1

Compound	R	R'	R''	R'''	pK_a
I	H	CH_3	CH_3	CH_3	10,8
II	CH_3	H	CH_3	CH_3	10,4
III	H	CH_3	C_2H_5	n-C_3H_7	11,1
IV	CH_3	H	C_2H_5	n-C_3H_7	10,4
V	H	CH_3	t-C_4H_9	H	10,9
VI	CH_3	H	t-C_4H_9	H	10,8

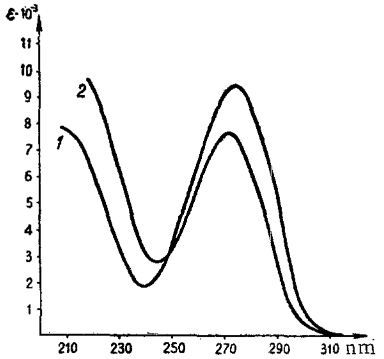


Fig. 1. UV spectrum of 1,5,6-trimethyluracil: 1) pH 2; 2) pH 12.

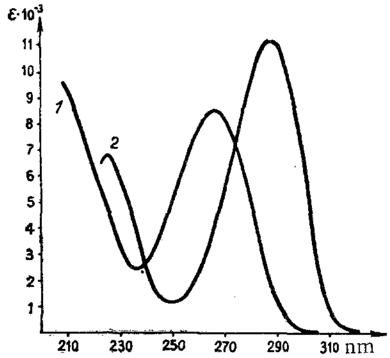


Fig. 2. UV spectrum of 3,5,6-trimethyluracil: 1) pH 2; 2) pH 14. (1 N NaOH).

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LITERATURE CITED

1. M. Draminski and B. Fiszer, Roczn. Chem., 43, 499, 1969.
2. M. Draminski and B. Fiszer, Roczn. Chem., 1970 (in press).
3. D. Shugar and J. J. Fox, Biochem. Biophys. Acta, 9, 199, 1952.
4. E. Wittenburg, Chem. Ber., 99, 239, 1966.
5. I. Wempen and J. J. Fox, J. Am. Chem. Soc., 86, 2474, 1964.
6. E. I. Stankevich, Yu. Yu. Popelis, E. E. Grinshtein, A. Ya. Ozola, and G. Ya. Dubur, KhGS [Chemistry of Heterocyclic Compounds], 6, 122, 1970.
7. A. Tóth and F. Billes, Acta Chim. Acad. Sci. Hung., 56, 229, 1968.