

HYDROLYSIS OF NUCLEOSIDES RELATED TO FLUORESCENT MINOR COMPONENTS  
OF PHENYLALANINE TRANSFER RIBONUCLEIC ACIDS

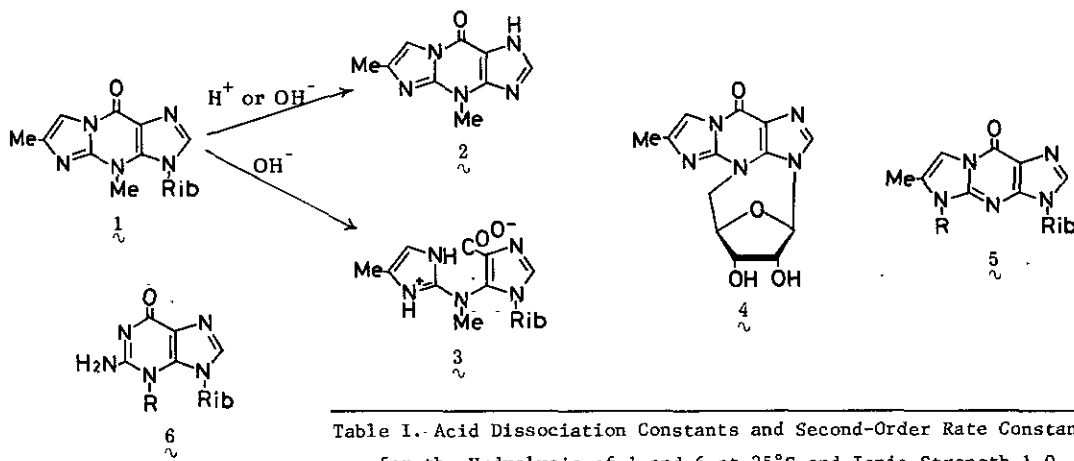
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The rates of hydrolysis of the glycosidic bond of 3- $\beta$ -D-ribofuranosylwe ( $1_{\sim}$ ), the most probable structure for wyosine from *Torulopsis utilis* tRNA<sup>Phe</sup>, were compared with those of the nucleosides ( $4_{\sim}$ ,  $5_{\sim}$ , and  $6_{\sim}$ ) structurally related to  $1_{\sim}$ . It has been found that the pseudo-first-order rate constants ( $k_{\text{obs}}$ ) for the hydrolysis of  $4_{\sim}$  and  $5a,b$  in 0.1 N HCl aq. at 85°C are of the same order of magnitude ( $6.3 \times 10^{-3}$ ,  $4.4 \times 10^{-3}$ , and  $3.3 \times 10^{-3} \text{ min}^{-1}$ , respectively) and that the hydrolysis of  $1_{\sim}$  at 25°C in 0.1 N HCl aq. ( $k_{\text{obs}} 4.4 \times 10^{-1} \text{ min}^{-1}$ ) takes place  $9.8 \times 10^5$  times as fast as that of  $5a$  and at a rate comparable to that of  $6b$  ( $k_{\text{obs}} 9.8 \times 10^{-1} \text{ min}^{-1}$ ). Acidic hydrolysis of  $1_{\sim}$  and  $6_{\sim}$  has been shown to proceed through their mono- and diprotonated species and the second-order rate constants ( $k_1$  and  $k_2$ ) are given in Table I. These results suggest that the partial structure  $6b$  in  $1_{\sim}$  is responsible for the unusual lability of  $1_{\sim}$  and steric assistance is one of the major effects of the 4-methyl group.

Compound  $1_{\sim}$  has also proved to undergo general-base-catalyzed hydrolysis to  $2_{\sim}$  and  $3_{\sim}$  competitively. However,  $1_{\sim}$  has been shown to be quite stable at pH 7.00 and 25°C for 40 days.



Rib =  $\beta$ -D-ribofuranosyl

- a: R = H
- b: R = Me
- c: R = Et
- d: R = Me<sub>2</sub>CH

Table I. Acid Dissociation Constants and Second-Order Rate Constants for the Hydrolysis of  $1_{\sim}$  and  $6_{\sim}$  at 25°C and Ionic Strength 1.0

Compound	pKa	$k_1$ (l mol <sup>-1</sup> min <sup>-1</sup> )	$k_2$ (l mol <sup>-1</sup> min <sup>-1</sup> )
$1_{\sim}$	3.06 ± 0.05	3.5	10
$6b_{\sim}$	3.99 ± 0.06	18	23
$6c_{\sim}$	3.86 ± 0.07	28	42
$6d_{\sim}$	3.83 ± 0.04	130	140