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

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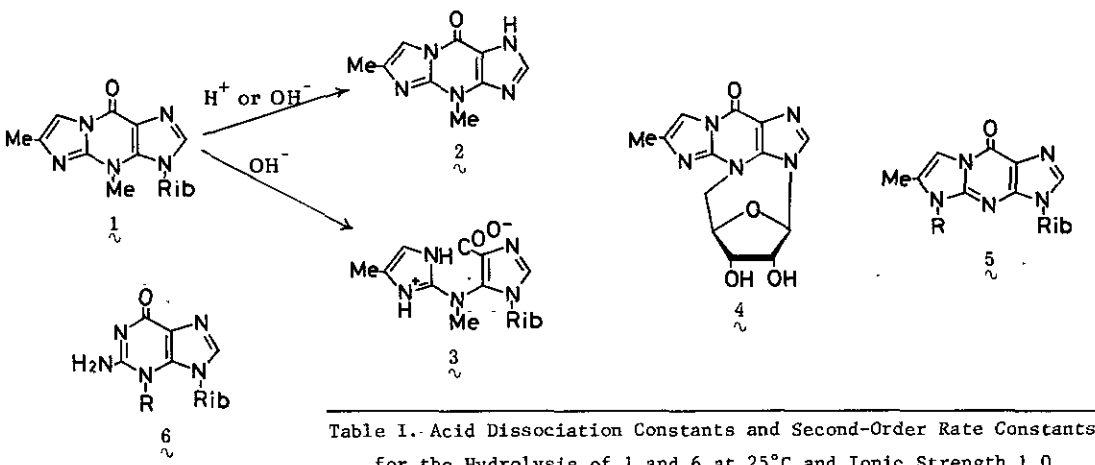
The rates of hydrolysis of the glycosidic bond of 3-β-D-ribofuranosylwye (1), the most probable structure for wyosine from Torulopsis utilis $tRNA^{Phe}$, were compared with those of the nucleosides (4, 5, and 6) structurally related to 1. It has been found that the pseudo-first-order rate constants (k_{obs}) for the hydrolysis of 4 and 5a,b in 0.1 N HCl aq. at 85°C are of the same order of magnitude (6.3×10^{-3}, 4.4×10^{-3}, and 3.3×10^{-3} min^{-1}, respectively) and that the hydrolysis of 1 at 25°C in 0.1 N HCl aq. (k_{obs} 4.4×10^{-1} min^{-1}) takes place 9.8×10^{5} times as fast as that of 5a and at a rate comparable to that of 6b (k_{obs} 9.8×10^{-1} min^{-1}). Acidic hydrolysis of 1 and 6 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 is responsible for the unusual lability of 1 and steric assistance is one of the major effects of the 4-methyl group.

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



Rib = β-D-ribofuranosyl

a: R = H
b: R = Me
c: R = Et
d: R = Me_2CH

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

Compound	pKa	k_1 ($l\ mol^{-1}\ min^{-1}$)	k_2 ($l\ mol^{-1}\ min^{-1}$)
1	3.06 ± 0.05	3.5	10
6b	3.99 ± 0.06	18	23
6c	3.86 ± 0.07	28	42
6d	3.83 ± 0.04	130	140