Hydrolysis of p-Nitrophenyl(deoxyguanylyldeoxyguanosine Succinate) by Deoxyguanylyldeoxyguanosine N-Acetylhistidate on Polycytidylic Acid

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For a study of a chemical reaction on a macromolecule, it is important to make clear a shape of the interaction of a reactant onto the macromolecule. The interaction between polyribonucleotide and oligodeoxyribonucleotide is specific and selective, although the magnitude of the interaction varies with its condition. In the present study, the shape of the interaction was investigated through the hydrolysis of p-nitrophenyl (deoxyguanylyldeoxyguanosine succinate) (I) by deoxyguanylyldeoxyguanosine N-acetylhistidate (II) on polycytidylic acid, Poly C, (III).

I and II were synthetized from di-p-methoxytrityldeoxyguanosine dimer.¹⁾ I contained 1.2 p-nitrophenyl group per molecule and II contained 0.9 imidazolyl group per molecule.

Figure 2 shows the hydrolyses of I by II with poly C and without poly C. The hydrolysis rate, R, was

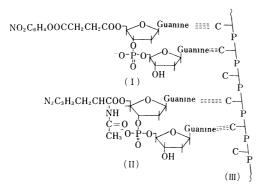


Fig. 1. Schematic diagram showing the hydrolysis of I by II on III.

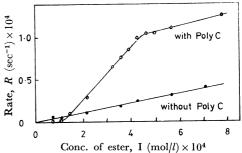


Fig. 2. Hydrolysis rates of I by II with and without Poly C.

○: presence of Poly C; 0.35 × 10⁻³ mol/l

•: absence of Poly C

0.01 M MgCl₂, 0.0001 M Mg(OAc)₂ pH=7.9; 5°C;

EtOH: H₂O=1: 100

I and II are the same concentrations.

defined as the increase of the hydrolyzed p-nitrophenol residue concentration per unit concentration of histidyl group, at the initial stage of the hydrolysis; R = [p-nitrophenol]/[N-acetylhistidine in II] $\cdot t$.

The hydrolysis does not occur when the ratio of I and II to poly C is less than 0.2, but it increases linearly with the ratio exceeding 0.3. When the ratio is over 1.3, the rate increasing with I in the presence of poly C is parallel to that in the absence of poly C.

It can be concluded that the interaction between the dinucleotide derivatives and poly C is statistically homogeneous at lower concentrations, so that the distance of two dinucleotide derivatives widens and no reaction takes place, and also that the shape of the interaction becomes heterogeneous with increase of the concentration of the dinucleotide derivatives so that the reaction takes place because of a successive lining up.

¹⁾ T. Shimidzu and R. L. Letsinger, J. Org. Chem., 33, 708 (1968).