

position inhabituelle mais la deuxième (vasopressine II) occupe la position de l'arginine-vasopressine des mammifères. Les tubes 170–200, contenant de la vasopressine I et les tubes 240–300, contenant la vasopressine II sont rassemblés, puis après élimination de l'acétate d'ammonium, les substances sont hydrolysées par HCl 6 N.

La vasopressine II possède la composition en acides aminés de l'arginine-vasopressine. La vasopressine I possède une composition voisine, mais le résidu de phénylalanine est remplacé par un résidu d'isoleucine. Cette nouvelle vasopressine possède une composition identique à celle d'un peptide synthétique, l'*arginine-vasotocine*, synthétisé par KATSOYANNIS ET DU VIGNEAUD⁵; comme ce dernier peptide, la nouvelle vasopressine possède une activité ocytotique secondaire relativement élevée si on la compare à l'activité vasopressique.

Cependant, une comparaison soigneuse des deux produits est nécessaire avant de conclure à une identité. Quoiqu'il en soit, la neurophysine du poulet, à la différence de celle des mammifères, contient 3 hormones neurohypophysaires de composition voisine.

*Laboratoire de Chimie Biologique, Faculté des Sciences,
Marseille (France)*

JACQUELINE CHAUVET
MARIE-THÉRÈSE LENCI
ROGER ACHER

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The effect of paramagnetic substances on the conversion of some pyrimidines by ultraviolet radiation

In previous papers^{1–6} we have reported upon the effects of ultraviolet radiation (2537 Å) on some components of nucleic acids in aqueous solution. A reversible hydration of uracil was known from the work of SINSHEIMER AND HASTINGS⁷. Moreover, long-continued irradiation leads to an irreversible destruction of these compounds. These reactions could be followed by the alterations of the ultraviolet spectra. We have found that besides these two photochemical phenomena, the pyrimidines show another reaction which is probably the most important. It appears that irradiation of aqueous solutions of the compounds, without any time lag, also brings about partial conversion into low-absorbing substances. The probable connection between this photochemical conversion and the lethal and mutagenic effects of ultraviolet radiation on micro-organisms has been suggested¹.

This reaction, which we have called "the first irreversible reaction" is remarkable because the extent to which it occurs appears limited to a specific percentage of the amount of the pyrimidine originally present (uracil, 6 %; thymine, 2 %; orotic acid, 13 %; cytosine, 3 %).

We have recently found a relationship between the amount of conversion and the oxygen concentration. Irradiation of an aq. solution of uracil saturated with O₂ brings

about a 3 % conversion, whereas expulsion of this gas, by bubbling through N_2 or H_2 , raises this percentage to 9–10 %. This oxygen effect is still more pronounced in the case of orotic acid (in O_2 -saturated solution, 7 %; after expulsion of O_2 , 35–37 %).

The occurrence of an equilibrium between orotic acid and its irradiation product could be demonstrated by the following experiments. If orotic acid is first irradiated for a short time in O_2 -free solution the absorbancy decreases about 35 %; saturating the solution with O_2 and repeating the irradiation causes a sharp rise of the absorbancy until a maximum is reached equal to about 7 % conversion of the orotic acid⁵. From these and other experiments⁵ we must conclude that the so called “first irreversible reaction” is by no means irreversible.

This remarkable effect of O_2 was supposed by us to be due to its paramagnetism⁴. If this assumption is correct it might be expected that all paramagnetic compounds will exert an effect on “the first irreversible reaction” similar to that of O_2 . This could be confirmed. Without any exception all paramagnetic ions tested (Cu^{++} , Co^{++} , Ni^{++} , Cr^{+++} , Mn^{++} and Fe^{++}) have shown the same effect on the equilibrium of “the first irreversible reaction” as O_2 . The experiments were performed in acid milieu to prevent salt formation. A solution of known concentration of orotic acid in 0.2 *N* HCl was saturated with N_2 and irradiated for 15 min. After addition of the metal-salt solution to a final concentration of $5 \cdot 10^{-3}$ *M*, the irradiation was repeated for 5 min. The paramagnetic ions brought about a partial recovery of the orotic acid, which had disappeared as a result of the first irradiation (orotic acid, 35–37 % decrease in absorbancy to 10–17 % decrease). Diamagnetic ions on the other hand (K^+ , Al^{+++} , Ca^{++} , Mg^{++} , Cd^{++} and Zn^{++}) were completely inert, the percentage converted in the first irradiation (35–37 %) remaining unchanged.

A quantitative relation between the concentration of a paramagnetic substance and the percentage of reversion was studied with Ni^{++} . Concentrations of $5 \cdot 10^{-3}$, $2.5 \cdot 10^{-3}$ and 10^{-3} *M* caused a rise in the absorbancy of the solutions corresponding to a reversion of the low-absorbing product from 35 % to 10 %, 16 % and 24 %, respectively.

Experiments similar to those described with orotic acid were also performed with uracil and generally the same results were obtained. However, no recovery of uracil could be found if the time between the two irradiations was too long. It is assumed that the reaction product of uracil is rather unstable. Some arguments can be given for this supposition.

The experiments with orotic acid strongly support our assumption that the rapid, seemingly irreversible, reactions lead to an equilibrium condition appropriate to the conditions of the ultraviolet irradiation. As soon as the irradiation is stopped this equilibrium is frozen. Changing of the conditions, *e.g.* by adding paramagnetic substances, results in a shift of the equilibrium under renewed irradiation. A reaction on a triplet level was supposed in one of our previous papers⁵. Singlet-triplet transitions are facilitated by paramagnetic molecules or ions. This will result in a lower concentration of the pyrimidine in the active form (triplet state) and consequently in a smaller amount of the irradiation product.

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*Biochemical Laboratory of the Technological University of Delft,
Delft (The Netherlands)*

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W. BERENDS

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