The discovery of natural hybrids should be of great interest also inasmuch as it is a hybrid male which is now the sole adult male in the troop and which has been the sole potential breeding male for some time. The female hybrid, although fully adult, appeared to have had no offspring thus far, as judged from the condition of her nipples.

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Solution Photochemistry of Thymine and Uracil

Abstract. *With dienes as specific triplet quenchers, it has been shown that the photodimerization of thymine in acetonitrile proceeds entirely through the triplet state and the photodimerization of uracil in acetonitrile or in water proceeds in part through the triplet state. The photohydration of uracil probably does not involve the triplet state. Efficiencies of intersystem crossing of thymine and uracil in acetonitrile were determined.*

We report here some observations concerning the mechanisms of the photochemistry of thymine and uracil in water (*1, 2*) and in acetonitrile. Photoreactions of both thymine and uracil were observed in degassed acetonitrile solutions at room temperature as judged by the disappearance of the characteristic ultraviolet absorption of the bases. The products in each case were dimers, as judged by infrared spectra (*3*), chromatographic properties (*3, 4*) and photoreversibility (*5*). The disappearance of substrate with irradiation time was examined for both thymine and uracil with and without added isoprene (*6, 7*).

The vertical triplet excitation energy for isoprene is 60 kcal/mole (*8*). The triplet energies of both thymine and uracil are greater than 70 kcal/mole (*9*). Thus isoprene should quench the triplet states of uracil and thymine at the diffusion-controlled rate. The bimolecular diffusion-controlled rate constant in acetonitrile near room temperature is about 10^{10} liter mole^{-1} sec^{-1}. Thus, at the lowest concentration of isoprene used ($0.7 \times 10^{-3}M$), virtually complete quenching of substrate triplets is expected if the triplets have lifetimes greater than about 10^{-5} second. Isoprene absorbs to the blue of uracil and thymine and thus is not expected to be an efficient quencher of their singlet states by an energy-transfer mechanism. Furthermore, even if there were singlet quenching processes which occur at the diffusion-controlled rate, the short lifetimes ($< 10^{-9}$ second) of the singlets (*10*) should preclude significant quenching by the isoprene at the concentrations used.

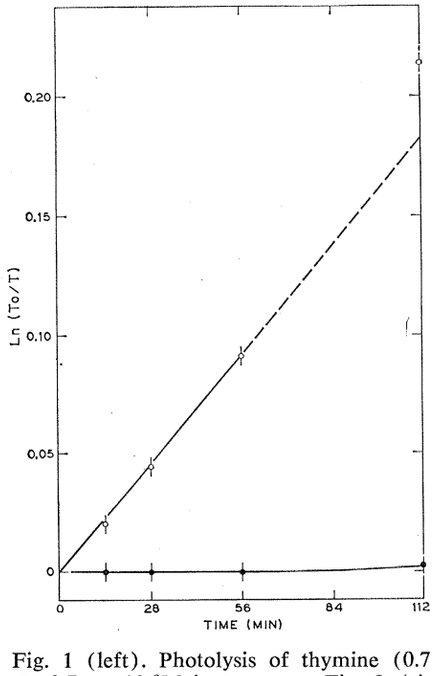
Typical results are shown in Figs. 1 and 2 which are graphs of first-order kinetics. Clearly, the photodimerizations of uracil and thymine in acetonitrile are quenched by small amounts of isoprene. With regard to thymine there is, for all intents and purposes, complete quenching. Therefore, we conclude that photodimerization of thymine in acetonitrile proceeds entirely by way of the triplet state. In the case of uracil there is a discontinuity. The reaction is incompletely quenched and furthermore a fourfold increase in isoprene concentration leads to the same amount of quenching. In addition, aeration gave the same results. Thus, we conclude that photodimerization of uracil proceeds by two mechanisms, and the path that is efficiently blocked by the isoprene involves the triplet state. It is not possible to decide at this time whether the unquenched uracil dimerization involves free uracil singlets.

Table 1. Triplet yields in acetonitrile, relative to that for triphenylene taken as 0.95 (*11*). Data obtained in degassed acetonitrile solution at room temperature; 2537-Å excitation; *cis*-piperylene concentration 0.01 to 0.05M.

Compound	Conc. ($10^{-3}M$)	Φisc
Thymine	2	0.18
Thymidine	2	.12
1,3-Dimethylthymine	2	.02
Uracil	1.3	.40
Uridine	1.8	.30
1,3-Dimethyluracil	4.0	.08

Initial quantum yields for the disappearance of substrate were measured as 0.05 for $0.7 \times 10^{-3}M$ uracil in degassed acetonitrile, and as 0.005 with isoprene present; about 0.005 for $0.7 \times 10^{-3}M$ thymine in acetonitrile; about 0.00 with isoprene present; about 0.01 for $10^{-3}M$ uracil in degassed water; about 0.000 for $10^{-3}M$ thymine in degassed water.

The quantum yields of thymine



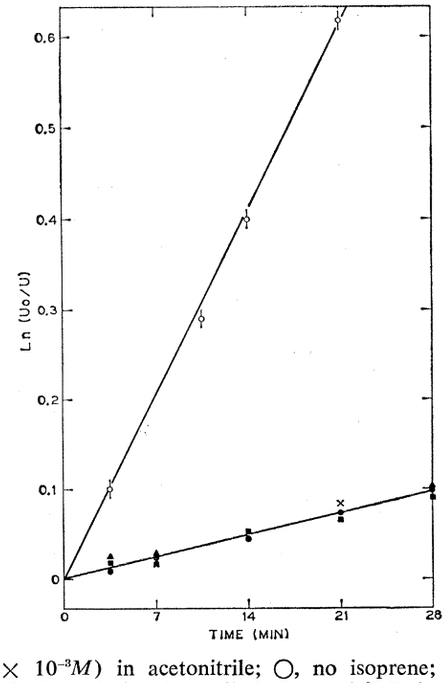


Fig. 1 (left). Photolysis of thymine ($0.7 \times 10^{-3}M$) in acetonitrile; ○, no isoprene; ● $0.7 \times 10^{-3}M$ isoprene. Fig. 2 (right). Photolysis of uracil ($0.7 \times 10^{-3}M$) in acetonitrile; ○ no isoprene; ▲ $0.7 \times 10^{-3}M$ isoprene; ● $1.5 \times 10^{-3}M$ isoprene; ■ $3.0 \times 10^{-3}M$ isoprene; X, air present.

Table 2. Photolysis of uracil in water. Identical doses of 260 to 300 mμ light in all cases; uracil concentration $10^{-4}M$; 2,4-hexadienol (HDE) concentration $10^{-4}M$; analyses by absorption spectrophotometry (addition of a small amount of mineral acid reverses the photohydration). Results are percentages.

	Degassed		Aerated	
	No HDE	HDE	No HDE	HDE
	Conversion			
	42±2	31±2	31±2	33±2
	Analysis of Products			
Hydrate	31±5	42±5	43±5	46±5
Dimers	69±5	58±5	57±5	54±5

and uracil triplets [Φisc (intersystem crossing)] obtained by 2537-Å excitation in acetonitrile solution were determined with *cis*-piperylene as the "triplet counter" (*11*). Note (Table 1) the reduction in yields when the hydrogen at the N-3 position of thymine or uracil is replaced by a methyl group. Phosphorescence from thymidine and uridine is observed only at high *p*H where the N-3 proton is removed (*9, 12*).

The difference in efficiencies of the dimerizations of thymine and uracil cannot be quantitatively accounted for on the basis of the difference in triplet yields. Steric hindrance afforded by the methyl group in thymine may be an important factor.

In water thymine undergoes a very slow photooxidation if the water solution is aerated (*13*). We observed no reaction of thymine in degassed water solution. On the other hand, photolysis of a water solution of uracil gives dimers and the photohydrate, the latter being detected by the heat and acid lability (*14*) of the material associated with the loss of absorbancy (Table 2). The initial ratio of hydrate to dimers decreases with increasing uracil concentration (*15*). In addition we found that the ratio depends on the presence or absence of air (oxygen) or of 2,4-hexadienol. The latter is a water soluble diene with a triplet energy of 59.5 kcal/mole (*16*) and is transparent at the wavelengths of the exciting light employed. The presence of air or 2,4-hexadienol leads to an increase in the ratio of hydrate to dimer. Furthermore, the disappearance of uracil is retarded by air or the hexadienol. Qualitatively, the data fits a model which does not involve the uracil triplet state in the photohydration reaction.

Paper chromatographic analysis and isolation by crystallization showed only one dimer from the photolysis of thymine in acetonitrile. This dimer has a different infrared spectrum and different chromatographic properties (*17*) from those the dimer produced by photolysis of DNA or of thymine in ice (*18*).

In addition to the dimer produced by photolysis of uracil in ice, a second dimer was isolated from photolyzed solutions of uracil in both water and acetonitrile. A qualitative examination has indicated that the ratio of "ice dimer" to new dimer increases in the presence of a triplet quencher. The stereochemical course of the photodimerization of coumarin depends on the excited state involved (*19*).

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6. Irradiations were carried out in a "merry-go-round" apparatus (*7*) which ensures all samples the same dose rate. Only wavelengths greater than 260 mμ were used and so the isoprene did not compete for exciting light. The exciting light intensity was the same for all runs, and all of the light impinging on the samples was absorbed.
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17. Samples spotted on Whatman No. 1 paper and chromatographed (descending) with a mixture of 1-butanol, water, and acetic acid (80 : 30 : 12, by volume); thymine "ice dimer" $R_F = 0.25$; thymine dimer produced in acetonitrile $R_F = 0.33$.
18. Photolysis of DNA or of thymine in ice gives the *cis*-"head-to-head" dimer. According to the assignments made by Weinblum and Johns (*3*) the dimer obtained here has the *trans*-"head-to-tail" structure.
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Evolution of Immunoglobulin Polypeptide Chains: Carboxy-Terminal of an IgM Heavy Chain

Abstract. *The dipeptide sequence at the carboxy-terminal of a heavy (μ) chain from a human macroglobulin (IgM) is tyrosylcysteine, although the reverse sequence, cysteinyltyrosine, has not been rigorously excluded. The presence of cysteine at the carboxy-terminal was predicted from a recognition of the chemical homologies among the polypeptide chains of immunoglobulins, and their probable evolutionary origin.*

On the basis of certain chemical similarities and amino acid sequence homologies between the light and heavy polypeptide chains of immunoglobulin molecules, Singer and Doolittle (*1*) have proposed that the cistrons coding for these two kinds of chain have evolved from a common ancestral gene. This proposal led to the specific prediction that at or near the carboxy-terminal of the IgM (immunoglobulin M) heavy chain (μ) there might be present a cysteine residue, since both classes of human light chains (κ and λ) have a cysteine residue in that region [carboxy-terminal for κ-chains (*2*); penultimate to carboxy-terminal for λ-chains (*3*)]. The heavy chains of IgG immunoglobulins (γ) do not have a cysteine residue in their carboxy-terminal region (*4*), although other homologies to the carboxy-terminals of light chains are apparent (*1*). In the light chains, these cysteines form part of the interchain disulfide link between the light and heavy chains (*3*). It was suggested, therefore, that such an evolutionarily conserved cysteine residue at the end of μ-chains might be responsible for the disulfide linkage of the five 7*S*-type subunits to form the 19*S* IgM molecule (*5*). To test this prediction we have treated a human μ-chain with carboxypeptidase A and have indeed found cysteine at the carboxy-terminal.

The IgM studied was a Waldenström