**MPM-A7**

**EFFECTS OF LIGHT ON FLUORINATED NUCLEIC ACIDS: PHOTOPRODUCT INDUCED CONFORMATIONAL CHANGES.**

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The effect of UV & visible light on nucleic acids (NA) and cellular DNA has been studied extensively(1). The present study deals with model NA containing 5-fluorouracil(F), a thymidine analogue used widely in cancer chemotherapy. Our earlier reports(2,3) have shown the kinetics of photodegradation of d-TpF, d-TPF and d-FpF, depending upon the pH, sensitized irradiation (sunlamps; phosphate buffer/acetonitrile), produces major degradation products which have been isolated and characterized: cis,syn dimer 5-5 adduct. The 5-5 adducts formed show some UV absorbance (268.9 nm max) compared to cis,syn which is indicative that the abnormal rings are partially saturated in 5-5 products. This feature is also evident in 1-D NMR spectra. Carbon-13 and proton coupled P-31 NMR spectra have been analyzed in this study. These analyses indicate: 1)C5=C6 of F[p] fragment in 5-5 is saturated while C5=C6 of [p]F fragment. 5-5 is not saturated; 2)Furanose conformation of F[p] fragment in cis FpT exists in C1-endo(2); C2'-twist(2T); in a ratio of 3:7, while [p]F fragment exists about equally in O4'-endo(0); C2'-endo(2E). Additional conformational features of these products will be presented.

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**MPM-A9**

**LONG RANGE ELECTRON TRANSFER IN METALLOAZURINS**

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Extended quenching of tryptophyl fluorescence in Cu(I)-azurin Pae was attributed to electron-transfer (Petrich et al. Biochem. 26:2711, 1987). To better define the mechanism for this extensive quenching, we investigated the fluorescence decay at 298K from azurins substituted with other metals. Replacement with Zn(I) caused only a small reduction in fluorescence lifetime to 4.3ns compared with metal free apoazurin Pae of 4.9ns. Reduction to form Cu(I)-azurin Pae increased the majority of the quenching from 100 ps with Cu(II) to 70ps. Replacement with Hg(II) decreased the quenching to 380ps. These observations are interpreted with Marcus theory for long-range electron transfer. The electron transfer rate for Cu(I) is near the maximum possible value, Hg(II) lies in the inverted region, Cu(II) lies in the normal region, near the maximum rate. The excited singlet state of tryptophyl residues cannot reduce Zn(II)-azurin Pae, which is consistent with expected reduction potentials. Substitution with Co(II) and Ni(II) also is associated with extensive quenching, though now in addition to electron-transfer there is considerable resonance dipole electronic energy transfer, which can be estimated from Forster's theory.

Metalloazurins Afe were investigated with Cu(I) and Hg(II) substitution. In each case the fluorescence decay was twofold greater. This arises in part from the tryptophyl residue in azurin Afe lying at the surface of the protein, exposed to water.