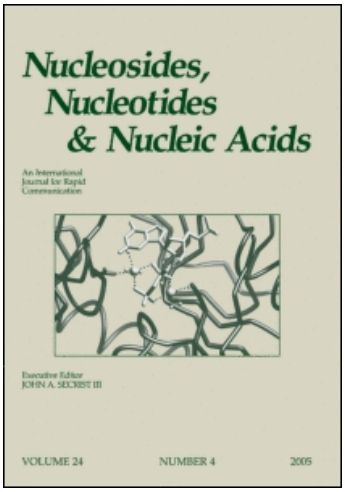

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A Zero-Length Diazirine Photoactive Nucleoside

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A Zero-Length Diazirine Photoactive Nucleoside

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ABSTRACT

The scheme of synthesis which allows to obtain 5-(3H-diazirin-3-yl)-2′-deoxyuridine as the zero-length photoactive nucleoside is described.

Nucleic acid analogs bearing a photoreactive diazirine moiety have been successfully used for photoaffinity labeling of proteins. A number of photoreactive nucleic acid analogs containing nucleotides, which were connected by different length spacers with diazirine group were synthesized and used for investigations of nucleic acid-protein interactions.[1,2] However, it is desirable to have a photoactive nucleoside with diazirine function of minimal length and volume. Cross-linking affected by this type reagent may be more selective and such photoprobe should be useful for structural analysis and for investigation of close contacts nucleic acid-protein.

We report the synthesis of a new photoactive derivative of deoxyuridine, which contain diazirine cycle at position 5 of the uracyl ring (I). The synthesis was carried out according to the scheme shown below, starting from dT (II). Acetyl groups were chosen for protecting hydroxyl sugar functions. Oxidation of the methyl group of the thymidine derivative (III) by potassium peroxydisulphate in the presence of catalytic amounts of copper ions in aqueous acetonitrile yielded 5-formyluridine (IV).[3] The Schiff's base (V) was prepared by the reaction of the aldehyde (IV) with *tert*-butylamine in dry dioxane in the presence of molecular sieves for 24 h at room

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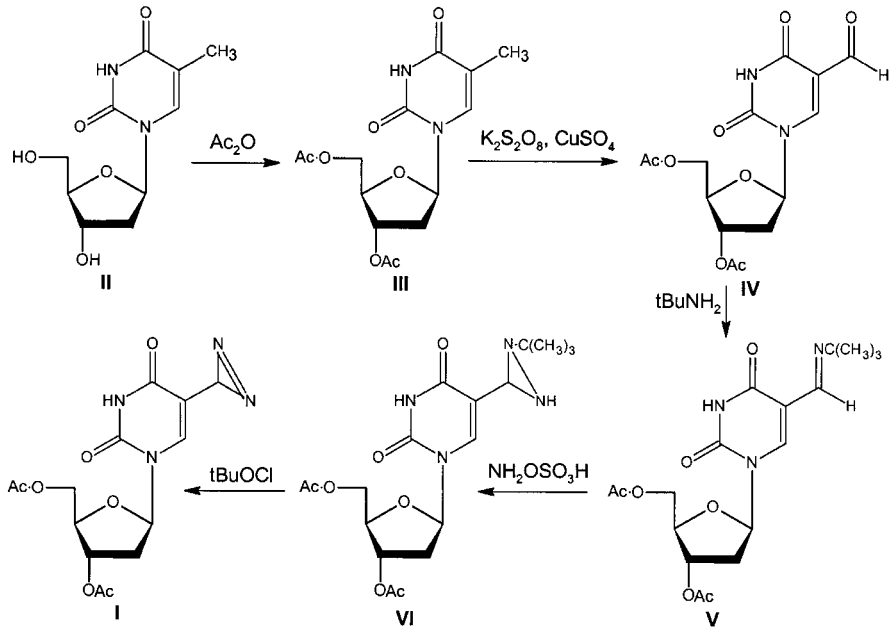

temperature. Formation of the diaziridine ring in compound (VI) was accomplished by the action of hydroxylamine-O-sulfonic acid in ethanol-water mixture (3:1) for 2–3 h at 0–4°C. Conversion of this intermediate (VI) to diazirine (I) was achieved by oxidation with tert-butylhypochlorite for 16 h at 0–4°C.[4] The presence of diazirine group in compound (I) was proved by thin layer chromatography. Under UV-light irradiation (366 nm) the spot corresponding to diazirine nucleoside formed the covalent bond with silicagel plate.

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