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A Novel Photoproduct of 2-Methoxycytosine in Phosphate Solution Under Far UV Irradiation

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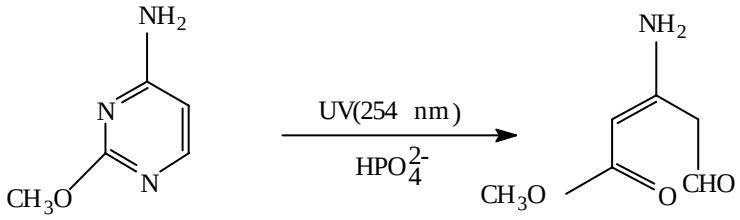
Abstract: Under the irradiation of medium pressure mercury lamp (MPML) the photolysis of 2-methoxycytosine (MAP) in phosphate solution leads to the production of a novel compound $C_5H_8N_3O_5P$. The composition and structure of the compound has been identified by elemental analysis, EI-MS, UV, IR, ^1H, ^{31}P-NMR.

Keywords: UV Photolysis, 2-methoxycytosine, phosphate.

The photolysis of 2-methoxycytosine in phosphate-buffer solution under low pressure mercury lamp (LPML, 254 nm) was reported as early as 1963 by Moor[1], who found that the presence of inorganic orthophosphate altered the course of the photolysis process of 2-methoxycytosine and produced an new compound **I (Scheme 1)**. Pith[2] and Shaw[3] confirmed the result of Moor, but the reaction mechanism had not been elucidated. In particular, the role of phosphate in the mechanism was not clear.

Scheme 1

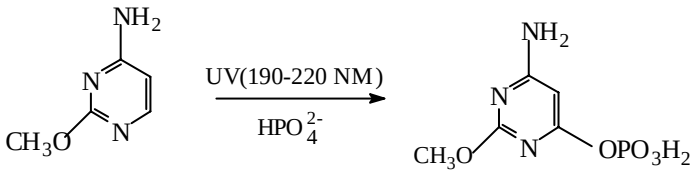


MAP **I**

In a previous paper[4] we found that the photolysis yield of nucleobases, nucleosides and nucleotides (NA) was sharply enhanced by phosphate undergoing MPML irradiation (continuous spectrum) and got a novel photoproduct (6-phosphatecytosine) in the photolytic system of cytosine-phosphate solution. Now we studied the photolysis of 1×10^{-4} mol/dm^3 2-methoxycytosine (MAP) in 0.05 mol/dm^3 phosphate solution by

irradiation of MPML and found the photolytic enhancement of MAP by added phosphate, which produced a novel compound **(Scheme 2)**

Scheme 2



MAP **II**

The compound **II** has been isolated and purified by anion-exchange resin. Analytic data of the compound are as following: Elemental analysis: $C_5H_8N_3O_5P$ Calcd: C: 27.15%, H: 3.62%, N: 19.01%, P: 14.02%, O: 36.20%, Found: C: 26.92%, H: 3.86%, N: 19.22%, P: 13.85%. EIMS: m/z $[M]^+$ 221 (22) , 169 (52), 140 (100), 84 (21), 57 (26), 31 (28); The ultraviolet spectrum of an aqueous solution of compound **II** at pH 7.0 exhibited two maxima at 274 nm and 208 nm, with the molar extinction coefficient 6.56 $\times 10^3$ and 2.32×10^4 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$ respectively. ^{1}H-NMR (500MHz, $CDCl_3$): δ ppm: 3.82 (s,3H), 7.81 (d, J=5 Hz, 1H); ^{31}P-NMR (85% H_3PO_4 as external standard $\delta = 0.80$): δ ppm: 0.81 (d, J=3Hz). Infrared absorption spectroscopy: ν : 3420, 3219, 1640, 1514, 1250,1163, 1122, 996, 960.

The analysis results have indicated that the possible structure of photo-product is identical to that of compound **II** (2-methoxy-6-phosphatecytosine). Filter experiments demonstrated that the wavelengths (190-220 nm) in the spectrum of MPML are responsible for the phosphate-induced enhancement. The possible mechanism of reaction **(Scheme 2)** is that HPO_4^{2-} absorbs the UV light (190-220 nm) of MPML and then forms phosphate anion radical $HPO_4^{-\bullet}$ [4-6], which reacts with MAP and produces compound **II**.

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References

1. A.M.Moor, *Can.J.Chem.*,**1963**,*41*,1973.
2. P.A.Show and G.C.Butler, *Can.J.Biochem.*,**1968**, *46*, 893.
3. A.A.Shaw and M.D.Shetler, *Photochem.photobiol.*,**1989**, *49*, 273.
4. F.Lin, W.Q.Wang and J.L.Wu, *Chem. Res. Chin.Univ.*, **1998**, *14*, 365.
5. M.Halmann and I.Platzner, *J.Chem. Soc.*, **1965**, 1440.
6. M.Halmann and I.Platzner, *J.Phys.Chem.*, **1967**, *71*, 1053.

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