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FORMATION OF N-1 SUBSTITUTED ALLOXAZINE DERIVATIVE FROM 7,8-DIMETHYL-10-FORMYLMETHYLISOALLOXAZINE IN ACETIC ACID.

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Abstract: The new alloxazine derivative formed from 7,8-dimethyl-10-formylmethylisoalloxazine in acetic acid has been isolated; structure and mechanism of formation have been proposed.

The degradation of 7,8-dimethyl-10-formylmethylisoalloxazine (FMF) in acetic acid is long known and used for the production of lumichrome (Lc).[1] We have found that in this reaction FMF does not decompose directly to Lc, but "via" an intermediate which exhibits already typical lumichrome-like absorption spectrum. This compound arising in a "dark" reaction was also found as a minor byproduct in photolysed solution of FMF in acetic acid.

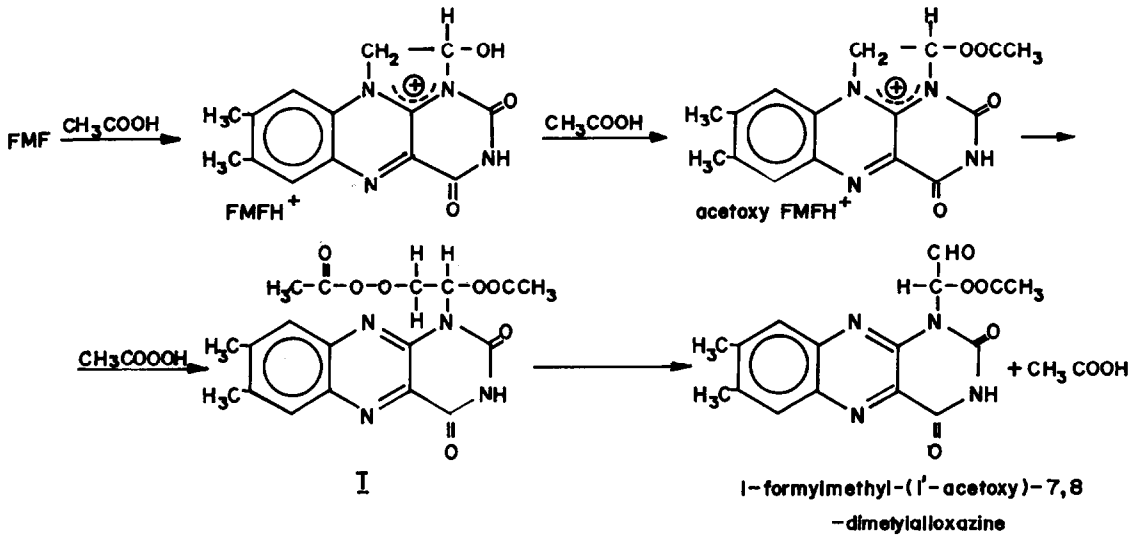
Synthesis of the intermediate: diluted solution of FMF in anhydrous acetic acid was refluxed for 1h (longer refluxing reduces the intermediate's yield). Solution containing the new compound and small amount of Lc was concentrared, precipitate was filtred off and recrystallized several times from acetic acid and next from chloroform. Immediately after recrystallization the compound is chromatographically pure but slowly decomposes to lumichrome.

Spectral properties of the intermediate: UV ViS (methanol) λ_{max} ($\varepsilon \times 10^3$) - 218 (35.5), 258 (33.3), 338 (9.1), 370 (7.2) nm, fluorescence spectrum in methanol (excited at 338 nm) - maximum at 463 nm, IR - strong band at 1757 cm^{-1} characteristic for carboxylic C=O, ^{1}H NMR ($CDCl_3$, δ): 9.77 (CHO, 1H,s) , 8.72 (broad multiplet, exchangeable) , 8.09 (C-6, 1H,s) , 7.81 (C-9, 1H,s) , 7.72 (C-1', 1H, s) , 2.54 (methyls at C-7 and C-8, 6H,s) , 2.34 (CH_3 from acetyl group, 3H,s) , molecular weight (m/e) - 342.

Based on the spectral properties we have proposed the intermediate structure as 1-formylmethyl-(1'-acetoxy)-7,8-dimethylalloxazine. The following evidence supports this structure:

1. Absorption and fluorescence spectra of the compound closely resemble those of Lc and its N-1 and/or N-3 derivatives.[2]
2. In the IR spectrum appears a strong band characteristic for a carbonyl of acetoxy group.
3. ^{1}H NMR spectrum indicates that intermediate contains formylmethyl and acetoxy groups.
4. The compound does not show phototautomerism what confirms substitution at N-1.[3]

5. The intermediate closely resembling FMF easily undergoes reaction with semicarbazide·HCl (new spots on TLC Rf = 0.47 for the intermediate and 0.25 for FMF) which indicates presence of an aldehyde group.[4]



Formation of the intermediate is probably caused by traces of peracetic acid. The compound does not form in acetic acid freshly distilled over $SnCl_2$. A small amount of peracetic acid added to purified acetic acid causes formation of the intermediate again. The same effect can be induced by flushing O_3 or irradiation at 253 nm of freshly distilled acetic acid, which seems to indicate that singlet oxygen is being involved.

Taking into account the above observation we can conclude that 1-formylmethyl-(1'-acetoxy)-7,8-dimethylalloxazine is formed from FMF by the formylmethyl group transfer from N-10 to N-1. The first step of this reaction probably consists of the acetylation of the free OH group of protonated FMF molecule. Then the bonding between N-10 and C-1' is broken by peracetic acid causing the formation of the labile peracetic species "I" which next decomposes to 1-formylmethyl-(1'-acetoxy)-7,8-dimethylalloxazine. As we have already mentioned 1-formylmethyl-(1'-acetoxy)-7,8-dimethylalloxazine is not stable either in solution or as crystals and can be easily converted to Lc by heating, irradiation and treatment with dilute acids or bases. Work is in progress for futher confirmation of the structure and mechanism of formation of the isolated intermediate.

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