

A NEW PRODUCT FROM THE DECOMPOSITION OF 2,4-DIHYDROXY-7-METHOXY-1,4-BENZOXAZIN-3-ONE (DIMBOA), A HYDROXAMIC ACID FROM CEREALS

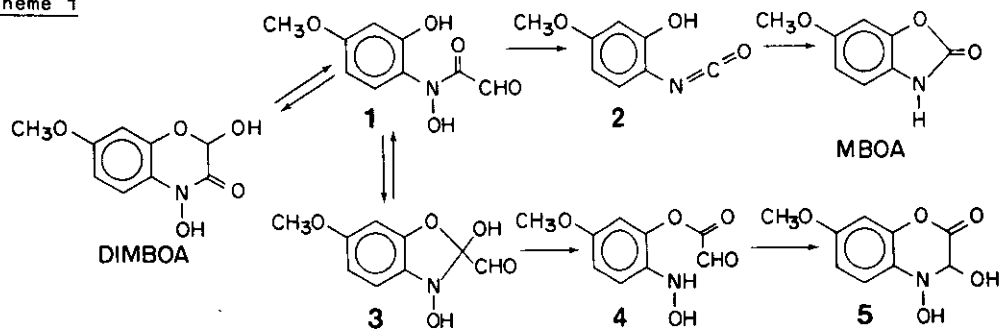
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Abstract- A new product, identified as 3,4-dihydroxy-7-methoxy-1,4-benzoxazin-2-one (5) was isolated in 10% yield from the decomposition of the title compound in dioxane. A mechanism for its formation is discussed.

Hydroxamic acids from cereal extracts, such as the title compound, DIMBOA, play an important defensive role in the plant.^{1,2} In interpreting the mode of action of DIMBOA at a molecular level, its chemistry in solution, in particular its decomposition reaction, has been of paramount importance.³ The reaction has been shown to give, as main product, 6-methoxy-benzoxazolin-2-one (MBOA), through the formation of the isocyanate 2 (Scheme 1).^{4,5} The yield of MBOA is not quantitative.⁶ We report herein the structure of a secondary product of the reaction, 5.

Scheme 1



The yield of MBOA from the decomposition of DIMBOA was dependent upon the basicity of the solvent system employed. In aprotic solvents, the logarithm of the yield correlated linearly ($r = 0.940$) with solvent donor number, a measure of the ability of the solvent to donate an electron pair.⁷ In aqueous solutions, the logarithm of the yield correlated linearly ($r = 0.996$) with pH (Fig. 1).

These results are consistent with the mechanism shown in Scheme 1. Thus, an increase in nucleophilicity of the hydroxamic hydroxyl group, either by interaction with an electron-donating solvent or by dissociation, would favor its attack on the aldehyde group of 1 with formation of intermediate 2.

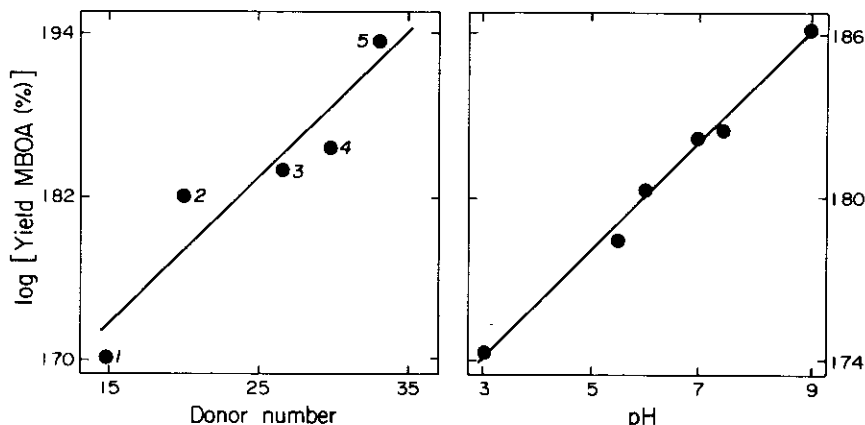


Fig. 1. Effect of donor number and pH on the yield of MBOA from the decomposition of DIMBOA in aprotic and aqueous solvents, respectively. DIMBOA was decomposed for at least 5 half-lives. Dioxane= 1, tetrahydrofuran= 2, N,N-dimethylformamide= 3, dimethylsulfoxide= 4, pyridine= 5.

Attempts to isolate secondary products were carried out in dioxane, the solvent producing the lowest yield of MBOA. DIMBOA was decomposed in dioxane at 63°C for 2 weeks. The residue was subjected to dry column flash chromatography and then to thin layer chromatography. A product with $R_f = 0.43$ (silica gel GF₂₅₄ with chloroform:methanol 10:1 as developing solvent), isolated in 10% yield, had the following properties: UV $\lambda_{\max}$ (EtOH) nm: 257, 287sh; $\lambda_{\max}$ (H₂O, pH 7) nm: 258 ($\epsilon = 15,400$), 285sh; $\lambda_{\max}$ (H₂O, pH 13) nm: 255sh, 300 ($\epsilon = 10,900$); $pK_a = 11.3$; IR $\nu_{\max}$ (KBr) cm^{-1} : 3200, 2950, 1665, 1610, 1500, 1460, 1280, 1140, 1080, 1020, 820; $^1\text{H-NMR}$ (60 MHz, CD_3OD) δ : 3.8 (3H,s, CH_3O), 5.5 (1H,s, CHOH), 6.4–7.0 (3H,m,aromatic); EIMS (probe, 70 eV) m/z (rel. int.): 211 (72) $[\text{M}]^+$, 182 (100) $[\text{M-CO-H}]^+$, 165 (39) $[\text{182-OH}]^+$, 153 (37) $[\text{M-CO-CHOH}]^+$, 137 (48) $[\text{153-O}]^+$, 122 (40) $[\text{153-NOH}]^+$, 106 (21) $[\text{122-O}]^+$; negative FeCl_3 test; positive Tollens' test. This data is consistent with structure 5, an isomer of DIMBOA. This product could be detected by thin layer chromatography in the decomposition mixture of DIMBOA in the other aprotic solvents studied.

The formation of 5 may be rationalized as shown in Scheme 1. The open form of DIMBOA, 1, may be demonstrated and quantified polarographically in aprotic solvents.⁸ Reclosure to hemiketal 3 has been proposed in the reactions of related compounds.⁹ Opening of 3 would follow to form 4 which would finally cyclize to yield 5 by addition of a hydroxylamine nitrogen to a carbonyl group, a reaction analogous to the well-known synthesis of hydroxamic acids.

The formation of 5 provides a rationalization of hitherto unexplained facts in the literature. Thus, the decrease of the yield of MBOA from DIMBOA as pH is lowered may be attributed to acid catalysis of the conversion of 3 to 4. Furthermore, the decomposition in strong acid of these hydroxamic acids has been reported to yield the corresponding 2-hydroxy-phenylhydroxylamine.¹⁰ Hydrolysis of ester 4 accounts for this product.

Other products from the reaction studied were coloured, resinous substances, which likely arise from oxidation and condensation of these intermediates.¹¹

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