# Analogues of the Cyclic Hydroxamic Acid 2,4-Dihydroxy-7-methoxy-2H-1,4-benzoxazin-3-one: Decomposition to Benzoxazolinones and Reaction with ?-Mercaptoethanol

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Analogues of the aglucones of naturally occurring cyclic hydroxamic acids (2,4-dihydroxy-1,4-benzoxazin-3-ones) from Gramineae (Poaceae) have been synthesized by the reductive cyclization of the ring-substituted methyl ?-(o-nitrophenoxy)-?-methoxyacetates, followed by demethylation of the C-2 methoxy group with BBr3 or BCl3 to reveal the 2-hydroxy group. A structure-activity series was produced by varying the substituent at C-7 on the aromatic ring [R = MeO (1), t-Bu (6), Me (7), H (8), Cl (9), F (10), C02Me (11a)]. The pKa, values for the hydroxamic acid and the phenol moieties were determined for each member of the C-7 series. They correlated well with ? in a linear free energy relationship (LFER) yielding values of p = 0.71 (with ?p) for pKa1 (the hydroxamic acid) and ? = 1.6 (with ?m) for pKa2 (the phenol). A LFER also existed between the rate constants for the unimolecular decomposition of these hydroxamic acids to benzoxazolinones and ?+ (?=-1.1). The rates of hydroxamic acid red