Halogenated Pyruvate Derivatives as Substrates of Transketolase from *Saccharomyces cerevisiae*

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Abstract—Pyruvate derivatives halogenated at C3 were shown to be donor substrates in the transketolase reaction. No drastic differences between the derivatives were observed in the value of the catalytic constant, whereas the Michaelis constant increased in the following order: Br-pyruvate < Cl-pyruvate < Cl_2-pyruvate < F-pyruvate < Br_2-pyruvate. The presence of the halogenated pyruvate derivatives increased the affinity of apotransketolase for the coenzyme; of note, the extent of this effect was equal with both of the active centers of the enzyme. In contrast, the presence of any other substrate known to date, including hydroxypyruvate (i.e. pyruvate hydroxylated at C3), induced nonequivalence of the active centers in that they differed in the extent to which the affinity for the coenzyme increased. Consequently, the β-hydroxyl of dihydroxyethylthiamine diphosphate (an intermediate of the transketolase reaction) played an important role in the phenomenon of nonequivalence of the active centers associated with the coenzyme binding. The fundamental possibility was demonstrated of using halogenated pyruvate derivatives as donors of the halogen-hydroxyethyl group in organic synthesis of halogenated carbohydrates involving transketolase.

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