Kinetic studies on the carboxylation of 6-amino-penicillanic acid to 8-hydroxy-penicilllic acid - DTU Orbit (08/12/2018)

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The carboxylation in aqueous solution of 6-amino-penicillanic acid (6-APA) to 8-hydroxy-penicilllic acid (8-HPA) was studied at 25 degrees C and pH 6.5. During sparging with either a citrate buffer or a chemically defined cultivation medium containing 6-APA with mixtures of carbon dioxide and air (2.7-41% (v/v) CO2), the kinetics for conversion of 6-APA was followed by HPLC. In the citrate buffer 6-APA was converted by two competitive reactions each following first order kinetics with respect to the concentration of 6-APA: 1. carboxylation into 8-HPA; and 2. slow conversion into an unknown compound. Formation of the unknown compound was not observed in the cultivation medium. The carboxylation of 6-APA was also found to be first order with respect to the concentration of dissolved carbon dioxide. The rate constant for formation of 8-HPA did not differ significantly in the cultivation medium compared to the citrate buffer. The kinetic was found to be the same at pH 5.0 and 6.5, and it is therefore concluded that it is dissolved carbon dioxide and not bicarbonate (or carbonate) that is involved in the carboxylation of 6-APA.

Attempts to identify the unknown compound in an incubation mixture of citrate and 6-APA by both NMR spectroscopy and HPLC revealed the presence of three new citrate-containing penicillins substituted at the amino position. Upon treatment with beta-lactamase one of the citrate-containing penicillins coeluted with the unknown compound. The unknown compound is most likely formed by hydrolysis of beta-lactam ring and eventually further chemical modifications of a citrate-containing penicillin. Copyright (C) 1996 Elsevier Science Ltd

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