## Hydrolysis of glycosylpyridinium ions by anomeric-configuration-inverting glycosidases Original Research Article

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### Abstract

The hydrolyses of five β-D-xylopyranosylpyridinium ions by the β-D-xylosidase of *Bacillus pumilus* proceed with $k_{cat}$ values $10^8$–$10^9$-fold larger than the rates of spontaneous hydrolysis of the same compounds. Log($k_{cat}$) values correlate well with aglycon p$K_a$ [$\beta_{lg}(V) = -0.52$, r = 0.99], whereas the correlation of log($k_{cat}/K_m$) is poor [r = 0.77; $\beta_{lg}(V/K) = \sim -0.6$]. The (1 → 3)-β-D-glucanase of *Sporotrichum dimorphosporum* hydrolyses 4-bromo-2-(β-D-glucopyranosyl)isoquinolinium ion with a rate enhancement of $10^8$. The amyloglucosidase II of *Aspergillus niger* hydrolyses three α-D-glucopyranosylpyridinium ions with rate enhancements of $10^5$–$10^8$. The efficient hydrolysis of glycosylpyridinium ions by these three inverting glycosidases, the catalytic mechanism of which is unlikely to involve a nucleophile from the enzyme, makes it imporable that the hydrolysis of glycosylpyridinium ions by retaining glycosidases discovered some years ago, is initiated by addition of a catalytic nucleophilic carboxylate group of the enzyme to the pyridinium ring.