



Houk-Jung Organic Colloquium

Atypical Reactions in the Biosynthesis of Herbicidins

Abstract: Herbicidins are adenosine-derived nucleoside antibiotics with an unusual tricyclic core structure. Deletion of the genes responsible for formation of the tricyclic skeleton in *Streptomyces* sp. L-9-10 reveals the in vivo importance of Her4, Her5 and Her6 during the early stages of herbicidin biosynthesis. In vitro characterization of Her4 and Her5 demonstrates their involvement in an initial, two stage C–C coupling reaction that results in net C5'-glycosylation of ADP/ATP by UDP/TDP-glucuronic acid. Biochemical analyses and intermediate trapping experiments imply a non-canonical mechanism of C-glycosylation reminiscent of NAD-dependent S-adenosylhomocysteine hydrolase. Structural characterization of the isolated metabolites suggested possible reactions catalyzed by Her6 and Her7, and subsequent biochemical experiments confirmed the functions of Her6 and Her7 as the C3' epimerase and C8' reductase, respectively. An overall herbicidin biosynthetic pathway is thus established based on these observations.

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Mani L. Bhuamik Collaboratory - YH 4222
Dongwon Yoo Seminar & Conference Hall

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