27O-ISMS14 **Bioinspired Chemical Synthesis of Monomeric and Dimeric Stephacidin A Congeners**

Ken MUKAI[1], Danilo PEREIRA DE SANT'ANA[1], ○Yasuo HIROOKA[2], Eduardo V. MERCADO-MARIN[1], David E. STEPHENS[1], Kevin G. M. KOU[1], Sven C. RICHTER[1], Naomi KELLEY[1], Richmond SARPONG[1]

[1]Department of Chemistry, University of California, Berkeley, [2]Ono Pharmaceutical Co., Ltd., Medicinal Chemistry Research Laboratories

Stephacidin A and its congeners are a collection of secondary metabolites that possess intriguing structural motifs. They stem from unusual biosynthetic sequences that lead to the incorporation of a prenyl or reverse-prenyl group into a bicyclo [2.2.2]diazaoctane framework, a chromene unit, or the vestige thereof. To complement biosynthetic studies, which normally play a significant role in unveiling the biosynthetic pathways of natural products, we demonstrated that chemical synthesis can provide important insights into biosynthesis. We achieved short total syntheses of congeners in the reverse-prenylated indole alkaloid family related to stephacidin A by taking advantage of a direct indole C6 halogenation of the related ketopremalbrancheamide. This novel strategic approach has now made possible the syntheses of several natural products, including malbrancheamides B and C, notoamides F, I and R, aspergamide B, and waikialoid A, which is a heterodimer of avrainvillamide and aspergamide B.