

## SUPPLEMENTARY INFORMATION

### 3-Ketoacyl-ACP Synthase (KAS) III Homologues and Their Roles in Natural Product Biosynthesis

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**Table S1.** KAS III enzymes in natural product biosynthesis

Enzyme	Natural Product	Percent sequence identity/similarity compared to <i>EcFabH</i>	Producer	Active Site Triad	Type of catalysis
DpsC	Daunorubicin	23/39	<i>Streptomyces peucetius</i>	Ser-His-Asp	C-C bond formation
AknE2	Aclacinomycin	25/39	<i>Streptomyces galilaeus</i> strain 3AR-33	Ser-His-Asp	C-C bond formation
BenQ	Benastatin	34/54	<i>Streptomyces</i> sp. A2991200	Cys-His-Asn	C-C bond formation
AlnI	Alnumycin	36/55	<i>Streptomyces</i> sp. CM020	Cys-His-Asn	C-C bond formation
ZhuH	R1128	40/57	<i>Streptomyces</i> sp. R1128	Cys-His-Asn	C-C bond formation
FrenI/FrnI	Frenolicin	37/54	<i>Streptomyces roseofulvus</i> strain AM-3867	Cys-His-Asn	C-C bond formation
FdmS	Fredericamycin	40/57	<i>Streptomyces griseus</i> ATCC 49344	Cys-His-Asn	C-C bond formation
HedS	Hedamycin	26/39	<i>Streptomyces griseoruber</i>	Ser-His-Asp	C-C bond formation
RedP	Undecylprodiginine	40/57	<i>Streptomyces coelicolor</i> M511	Cys-His-Asn	C-C bond formation
NzsF	Neocarazostatin	42/58	<i>Streptomyces</i> sp. strain MA347	Cys-His-Asn	C-C bond formation
AsuC3	Asukamycin	35/51	<i>Streptomyces nodusus</i> subsp. <i>asukaensis</i>	Cys-His-Asn	C-C bond formation
AsuC4	Asukamycin	40/56	<i>Streptomyces nodusus</i> subsp. <i>Asukaensis</i>	Cys-His-Asn	C-C bond formation

SalQ/Orf12	Salinomycin	38/55	<i>Streptomyces albus</i> XM211	Cys-His-Asn	C-C bond formation
TcsB	FK506	no identity seen with EcFabH	<i>Streptomyces</i> sp. KCTC 11604BP	Not reported	C-C bond formation
RevR	Reveromycin	38/55	<i>Streptomyces</i> sp. SN-593	Cys-His-Asn	C-C bond formation
PqsBC	Alkylquinolone	PqsB: 25/37 (amino acids 24-125) PqsC: 21/40	<i>Pseudomonas aeruginosa</i> PAO1	PqsB: No conserved triad PqsC: Cys-His	C-C bond formation
PqsD	Alkylquinolone	39/56	<i>Pseudomonas aeruginosa</i> PAO1	Cys-His-Asn	C-C bond formation
CorB	Corallopyronin	33/48	<i>Corallocooccus coralloides</i> strain B035	Cys-His-Asn	C-C/C-O (ester) bond formation
MxnB	Myxopyronin	31/48	<i>Myxococcus fulvus</i> strain Mxf50	Cys-His-Asn	C-C /C-O (ester) bond formation
PpyS	Photopyrone	28/46 (amino acids 2-149)	<i>Pseudomonas putida</i> BW11M1	Cys-His-Asn	C-C bond formation
DarB	2,5-Dialkylresorcinol	22/34	<i>Pseudomonas aurantiaca</i> BL915	Cys-His-Asn	C-C bond formation
LstAB	Lipstatin	LstA: 24/39 (amino acids 28-124) LstB: 32/46 (amino acids 11-189)	<i>Streptomyces toxytricini</i>	LstA: Cys-His-Asn LstB: no conserved triad	C-C bond formation
RkD	RK-682	32/46 (amino acids 11-189)	<i>Streptomyces</i> sp. 88-682	Cys-Xxx-Xxx	C-C /C-O (ester) bond formation
AbyA1	Abyssomicin	28/44	<i>Verrucosispora maris</i> AB-18-032	Cys-Xxx-Xxx	C-C /C-O (ester) bond formation
Tmn15	Tetronomycin	27/43	<i>Streptomyces</i> sp. NRRL 11266	Cys-Xxx-Xxx	C-C /C-O (ester) bond formation
KijB	Kijanimicin	31/47 (amino acids 59-301)	<i>Actinomadura kijaniata</i> SCC1256	Cys-Xxx-Xxx	C-C /C-O (ester) bond formation
NphT7	Mevalonate/Terpenoid	36/54	<i>Streptomyces</i> sp. strain CL190	Cys-His-Asn	C-C bond formation
ThgI	Trehangelin	39/58	<i>Polymorphospora rubra</i> K07-0510	Cys-His-Asn	C-C bond formation
SsfN	Tetracycline SF2575	35/53	<i>Streptomyces</i> sp. SF2575	Cys-His-Asn	C-C bond formation
CerJ	Cervimycin	23/36	<i>Streptomyces tendae</i> strain HKI 017	Cys-His-Asp	C-O bond (ester)formation
ChIB3	Chlorothricin	23/38	<i>Streptomyces antibioticus</i> DSM 4072	Cys-His-Asp	trans thio-esterification to ChIB2
ChIB6	Chlorothricin	30/39 (amino acids 46-177)	<i>Streptomyces antibioticus</i> DSM 4072	Cys-His-Asp	C-O bond (ester) formation
PtmR	Pactamycin	25/37 (amino acids 8-157)	<i>Streptomyces pactum</i> strain ATCC 27456	Cys-His-Asp	C-O bond (ester) formation

AviN	Avilamycin	no identity seen with EcFabH	<i>Streptomyces viridochromogenes</i> Tü57	Cys-Thr-Asp	C-O bond (ester) formation
Evrl	Evernimicin	21/38 (amino acids 39-189)	<i>Micromonospora carbonacea</i>	Cys-Thr-Asp	C-C bond formation
CalO4	Calicheamicin	26/40	<i>Micromonospora echinospora</i> NRRL 15839	Cys-His-Asp	C-S bond (thioester) formation
TiaF	Tiacumicin	21/39	<i>Dactylosporagium aurantiacum</i> subsp. hamdenensis NRRL 18085, <i>Actinoplanes deccanensis</i>	Cys-His-Asp	C-O bond (ester) formation
EsmD1	Esmeraldin	21/38 (amino acids 8-171)	<i>Streptomyces antibioticus</i> Tü 2706	Cys-His-Asp	C-O bond (ester) formation
BomK	A33853	25/37 (amino acids 10-178)	<i>Streptomyces</i> sp. NRRL12068	Cys-His-Asp	C-N (amide) bond formation