# *Perkin 1 Abstracts:* Natural Product Synthesis

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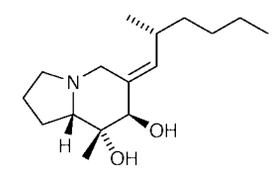
*Perkin 1 Abstracts: Natural Product Synthesis* aims to highlight syntheses that have been recently published. It includes brief descriptions of *biological activity* and *key steps*. A more comprehensive list of Natural Product syntheses and isolations can be found in *Natural Product Updates*

### (+)-Allopumiliotoxin

*Biological activity*: not reported.

*Key steps*: simultaneous construction of the 6-membered ring, trisubstituted alkene and a stereogenic centre (2° alcohol) by intramolecular Ni-catalysed reductive cyclisation of an ynal.

X.-Q. Tang and J. Montgomery, *J. Am. Chem. Soc.*, 1999, **121**, 6098.

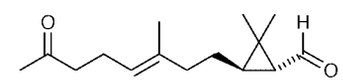



### (–)-Anthoplalone

*Biological activity*: antitumour activity against murine melanoma cells (22μg/mL).

*Key steps*: Julia olefination.

S. Hanessian, L.-D. Cantin and D. Andreotti, *J. Org. Chem.*, 1999, **64**, 4893.

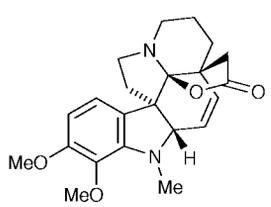



### Aspidophytine

*Biological activity*: the title compound is a constituent of an insecticidal powder prepared from the dried leaves of the Mexican plant *Haplophyton cimicidum*.

*Key steps*: (a) generation of 4 rings in one step from a tryptamine and an acyclic dialdehyde bearing an allylsilane *via* a dihydropyridinium intermediate; (b) all stereochemistry derived from an allylic alcohol generated by CBS reduction.

F. He, Y. Bo, J. D. Altom and E. J. Corey, *J. Am. Chem. Soc.*, 1999, **121**, 6771.

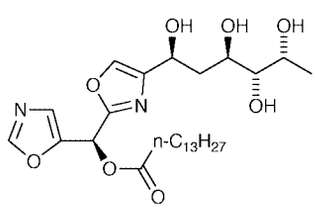



### Bengazole A

*Biological activity*: potent *in vitro* antifungal activity against *Candida albicans*.

*Key steps*: (a) sequential two-stage grafting of side chains to the central oxazole ring with tight control of regioselectivity; (b) addition of an aldehyde to a C4-metallated oxazole with chelation-controlled stereoselectivity; (c) modified Vedejs borane-mediated lithiation-aldehyde addition at the C2 position of the oxazole.

R. J. Mulder, C. M. Shafer and T. F. Molinski, *J. Org. Chem.*, 1999, **64**, 4995.

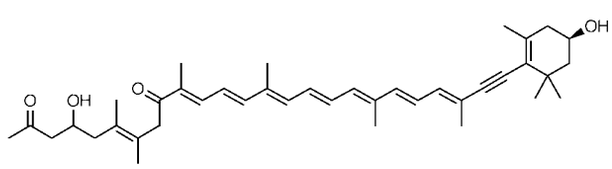



### Crassostreaxanthin B

*Biological activity*: isolated from *Crassostrea gigas*; biological activity not reported.

*Key steps*: Lewis-acid mediated cleavage of a tetrazole cyclohexane epoxide to an acyclic tetrasubstituted alkene.

C. Tode, Y. Yamano and M. Ito, *J. Chem. Soc., Perkin Trans. 1*, 1999, 1625.

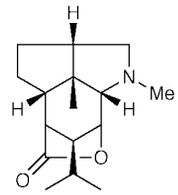


## (–)-Dendrobine

*Biological activity*: antipyretic and antihypotensive.

*Key steps*: (a) intramolecular N–C bond formation by addition of a carbamyl radical to the alkene of verbenol generates an oxazoldinone after fragmentation of the cyclobutane ring; (b) intramolecular Pauson–Khand reaction to generate two five-membered rings and a quaternary centre.

J. Cassayre and S. Z. Zard, *J. Am. Chem. Soc.*, 1999, **121**, 6072.

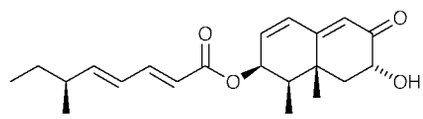



## Dendryphiellin C

*Biological activity*: not reported.

*Key steps*: Robinson annulation.

H. Akao, H. Kiyota, T. Nakajima and T. Kitahara, *Tetrahedron*, 1999, **55**, 7757.

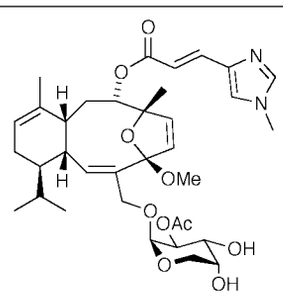



## Eleutherobin

*Biological activity*: potent antitumour properties with taxol-like mechanism of action; i.e. causes tubulin polymerisation and stabilises microtubules.

*Key steps*: (a) Nozaki-Kishi ring closure to produce the furanophane, (b) transposition of a pyranose to a furanose; (c) Pd(0)-catalysed methoxycarbonylation of a vinyl triflate to give an allylic alcohol.

X.-T. Chen, S. K. Bhattacharya, B. Zhou, C. E. Gutteridge, T. R. R. Pettus and S. J. Danishefsky, *J. Am. Chem. Soc.*, 1999, **121**, 6563.

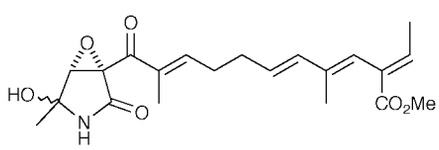



## (+)-Epolactaene

*Biological activity*: neuritogenic agent.

*Key steps*: *E*-selective Wittig reaction.

S. Marumoto, H. Kogen and S. Naruto, *Tetrahedron*, 1999, **55**, 7145.

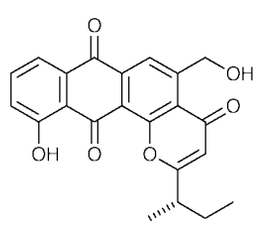



## (*S*)-Espicufolin

*Biological activity*: neuronal cell-protecting substance.

*Key steps*: intramolecular acyl-transfer.

H. Uno, K. Sakamoto, E. Honda and N. Ono, *Chem. Commun.*, 1999, 1005.

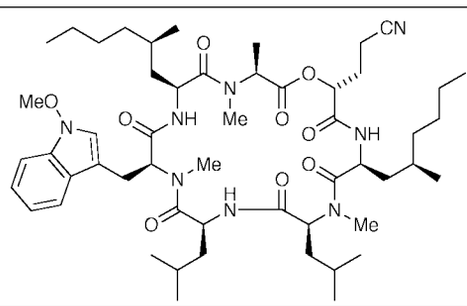



## HUN-7293

*Biological activity*: potent inhibitor of cell adhesion molecule expression exhibiting anti-inflammatory properties.

*Key steps*: unusually efficient macrocyclisation with the formation of the *N*-methyl Leu-Leu secondary amide resulting from H-bonding assisted pre-organisation.

D. L. Boger, H. Keim, B. Oberhauser, E. P. Schreiner and C. A. Foster, *J. Am. Chem. Soc.*, 1999, **121**, 6197.

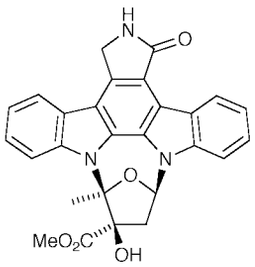


## (+)-K252a

*Biological activity*: inhibitor of protein kinase C.

*Key steps*: (a) non-oxidative photocyclisation to generate the indolocarbazole; (b) *N*-cycloglycosidation by electrophilic addition of a carbazole NH to an α-methylene tetrahydrofuran mediated by iodine.

Y. Kobayashi, T. Fujimoto and T. Fukuyama, *J. Am. Chem. Soc.*, 1999, **121**, 6501.

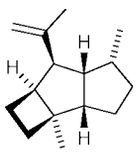


## Kelsoene

*Biological activity*: not reported.

*Key steps*: one carbon homologation through Wittig reaction.

G. Mehta and K. Srinivas, *Tetrahedron Lett.*, 1999, **40**, 4877.

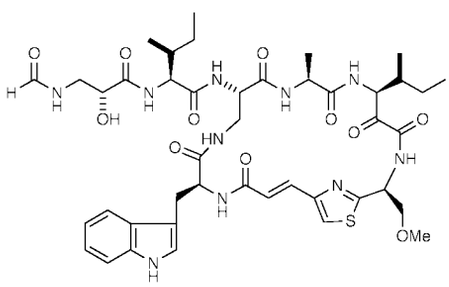


## Keramamide

*Biological activity*: (a) cytotoxic; (b) anti-fungal; (c) anti-oxidant.

*Key steps*: (a) Wittig olefination; (b) reduction under Luche conditions; (c) oxidation under Sharpless conditions; (d) Staudinger reduction of an azide.

J. A. Sowinski and P. L. Toogood, *Chem. Commun.*, 1999, 981.

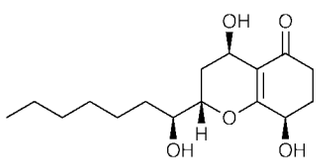


## (+)-Koninginin D

*Biological activity*: not reported.

*Key steps*: condensation of an aldehyde and cyclohexane-1,3-dione by a method described by Paquette using thiophenol, and $SiO_2$.

G. Liu and Z. Wang, *Chem. Commun.*, 1999, 1129.

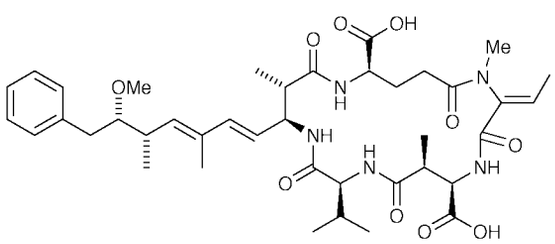


## Motuporin

*Biological activity*: inhibitor of protein phosphatase 1 and 2A.

*Key steps*: (a) Ugi's four-component condensation reaction to synthesize the 2-*N*-methylaminobutenyl residue; (b) Matteson's 1,2-metallate rearrangement using a homochiral boronate and dihalomethyllithium to synthesize an α-amino acid.

S. M. Bauer and R. W. Armstrong, *J. Am. Chem. Soc.*, 1999, **121**, 6355.

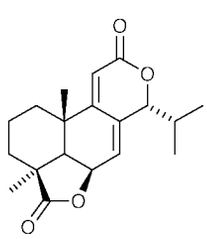


## Nagilactone F and LL-Z1271α

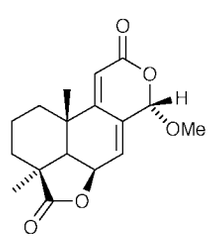
*Biological activity*: potent allelopathic activity.

*Key steps*: routine methods were employed.

A. F. Barrero, J. F. Sánchez, J. Elmerabet, D. Jiménez-González, F. A. Macías and A. M. Simonet, *Tetrahedron*, 1999, **55**, 7289.



Nagilactone F



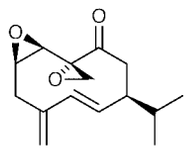
LL-Z1271α

## (–)-Periplanone B

*Biological activity*: sex attractant of the American cockroach.

*Key steps*: ring-closure alkene metathesis.

D. M. Hodgson, A. M. Foley and P. J. Lovell, *Synlett*, 1999, 744.

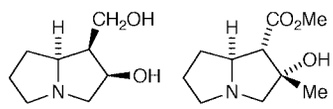


## (–)-Petasinecine and Tussilagine

*Biological activity*: not reported.

*Key steps*: Mitsunobu reaction.

D. Ma and J. Zhang, *J. Chem. Soc., Perkin Trans. 1*, 1999, 1703.



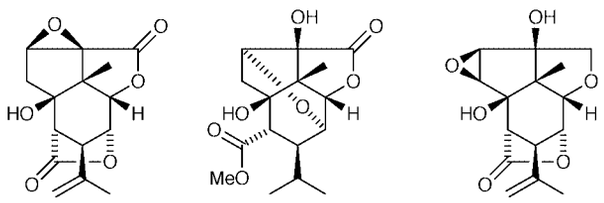
(–)-Petasinecine Tussilagine

## Picrotoxinin, Methyl Picrotoxate, Corianin

*Biological activity*: picrotoxinin is a potent and specific antagonist of the neurotransmitter suppressor γ-aminobutyric acid (GABA) and it inhibits the opening of chloride ion channels *in vivo*.

*Key steps*: intramolecular Pd(0)-catalysed Alder-ene reaction.

B. M. Trost and M. J. Krische, *J. Am. Chem. Soc.*, 1999, **121**, 6131. See also B. M. Trost, C. D. Haffner, D. J. Jebaratnam, M. J. Krische and A. P. Thomas, *J. Am. Chem. Soc.*, 1999, **121**, 6183.



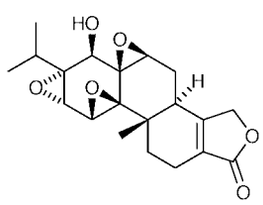
Picrotoxinin Methyl Picrotoxate Corianin

## (–)-Triptolide

*Biological activity*: antitumour and immunosuppressive agent isolated from the Chinese medicinal plant *Tripterygium wilfordii* Hook F.

*Key steps*: enantioselective $Mn(OAc)_3$-mediated oxidative radical cyclisation catalysed by $Yb(OTf)_3$. Related compunds (–)-triptonide and (+)-triptophenolide were synthesised by similar methods.

D. Yang, X.-Y. Ye, S. Gu and M. Xu, *J. Am. Chem. Soc.*, 1999, **121**, 5579.

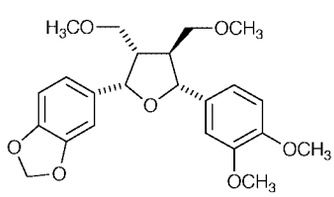


## (–)-Virgatusin

*Biological activity*: inhibits the endogenous DNA polymerase of hepatitis B virus (HBV).

*Key steps*: (a) addition of an organolithium reagent to a functionalised lactone; (b) asymmetric deoxygenation of an hemiketal intermediate.

H. Yoda, M. Mizutani and K. Takabe, *Tetrahedron Lett.*, 1999, **40**, 4701.



## Volicitin

*Biological activity*: elicitor of plant volatile biosynthesis from beet armyworm salivary secretion.

*Key steps*: three component one-pot double-Wittig reaction.

G. Pohnert, T. Koch and W. Boland, *Chem. Commun.*, 1999, 1087.