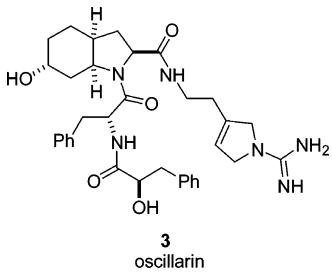


Total Synthesis and Structural Confirmation of Chlodorodysinosin A [J. Am. Chem. Soc. 2006, 128, 10491–10495]. Stephen Hanessian,* Juan R. Del Valle, Yafeng Xue, and Niklas Blomberg

Page 10492. In Figure 1, the structure of oscillarin (**3**) was incorrect. The correct structure is shown below:



Page 10493. In Scheme 1, for **7b**, R should be SO_2PhMe .

Due to a production error, the references following ref 21 were misnumbered in the version of this paper published on the Web July 24, 2006 (reflecting a change to Figure 1 after initial ASAP publication on July 21, 2006), and in the August 16, 2006 issue.

The electronic version of this paper, with the correct Figure 1 and Scheme 1 and the references correctly numbered, was replaced on the Web on August 22, 2006.

The complete list of references, correctly numbered, is presented below.

References

- (1) For recent reviews on cyanobacterial metabolites, see: (a) Burja, A. M.; Banaigs, B.; Abou-Mansour, E.; Burgess, L. G.; Wright, P. C. *Tetrahedron* **2001**, *57*, 9347. (b) Leusch, H.; Harrigan, G. G.; Goetz, G.; Horgen, F. D. *Curr. Med. Chem.* **2002**, *9*, 179. (c) Shiori, T.; Hamada, Y. *Synlett* **2001**, 184. (d) Lewis, J. R. *Nat. Prod. Rep.* **1998**, 417. (e) Namikoshi, M.; Rinehart, K. L. *Indust. Microbiol.* **1996**, *17*, 373. (f) Rinehart, K. L.; Namikoshi, M.; Choi, B. W. *J. Appl. Phycol.* **1994**, *6*, 159.
- (2) (a) Colman, R. W.; Clowes, A. W.; George, J. N.; Hirsh, J. L.; Marder, J. V. In *Overview of Homeostasis*, 4th ed.; Colman, R. W., Hirsh, J. L., Marder, J. V., Clowes, A. W., George, J. N., Eds.; Hemostasis and Thrombosis: Basic Principles and Clinical Practice; Lippincott Williams & Wilkins: Philadelphia, 2001; p 3. (b) Dahlbäck, B. *Lancet* **2000**, *355*, 1627. (c) Steinmetz, T.; Hauptman, J.; Stürzebecher, J. *Exp. Opin. Invest. Drugs* **2000**, *10*, 845. (d) Kimball, S. D. *Blood Coagul. Fibrinol.* **1995**, *6*, 511.
- (3) For selected reviews on thrombin inhibitors, see: (a) Sanderson, P. E.; Nayler-Olson, A. M. *Curr. Med. Chem.* **1998**, *5*, 289. (b) Ripka, W. E. *Curr. Opin. Chem. Biol.* **1997**, *1*, 242. (c) Pfau, R. *Curr. Opin. Drug Discovery* **2003**, *6*, 437.
- (4) (a) Hanessian, S.; Therrien, E.; van Otterlo, W. A. L.; Bayrakdarian, M. A.; Nilsson, I.; Fjellström, O.; Xue, Y. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 1032. (b) Hanessian, S.; Tremblay, M.; Marzi, M.; Del Valle, J. R. *J. Org. Chem.* **2005**, *70*, 5070. (c) Hanessian, S.; Sailes, H.; Therrien, E. *Tetrahedron* **2003**, *59*, 7047. (d) Hanessian, S.; Balaux, E.; Musil, D.; Olsson, L.-L.; Nilsson, I. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 243. (e) Hanessian, S.; Therrien, E.; Granberg, K.; Nilsson, I. *Bioorg. Med. Chem. Lett.* **2000**, *12*, 2907.
- (5) (a) Liu, Z.; Ranier, J. D. *Org. Lett.* **2006**, *8*, 459. (b) Nie, X.; Wang, G. *J. Org. Chem.* **2005**, *70*, 8687. (c) Fukuta, Y.; Ohshima, T.; Gnanadesikan, V.; Shibuguchi, T.; Nemoto, T.; Kisugi, T.; Okino, T.; Shibasaki, M. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5433. (d) Toyooka, N.; Nakazawa, A.; Himiyama, T.; Nemoto, H. *Heterocycles* **2003**, *59*, 75. (e) Toyooka, N.; Okumura, M.; Himiyama, T.; Nakazawa, A.; Nemoto, H. *Synlett* **2003**, *55*. (f) Valls, N.; Vallribera, M.; Font-Bardia, M.; Solans, X.; Bonjoch, J. *Tetrahedron: Asymmetry* **2003**, *14*, 1241. (g) Radau, G.; Stürzebecher, J. *Pharmazie* **2002**, *57*, 11. (h) Radau, G.; Rauh, D. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 779. (i) Bonjoch, J.; Catena, J.; Isábal, E.; López-Canet, M.; Valls, N. *Tetrahedron: Asymmetry* **1996**, *7*, 1899.
- (6) (a) Aeruginosin 298A: Murakami, M.; Okita, Y.; Matsuda, H.; Okino, T.; Yamaguchi, K. *Tetrahedron Lett.* **1994**, *35*, 3129. (b) Aeruginosins 98A and 98B: Murakami, M.; Ishida, K.; Okino, T.; Okita, Y.; Matsuda, H.; Yamaguchi, K. *Tetrahedron Lett.* **1995**, *36*, 2785. (c) Aeruginosins 102A and 102B: Matsuda, H.; Okino, T.; Murakami, M.; Yamaguchi, K. *Tetrahedron* **1996**, *52*, 14501. (d) Aeruginosins 205A and 205B: Shin, H. J.; Matsuda, H.; Murakami, M.; Yamaguchi, K. *J. Org. Chem.* **1997**, *62*, 1810. (e) Oscillarin: Engh, R.; Konetschny-Rapp, S.; Krell, H.-W.; Martin, U.; Tsakalidis, C. PCT WO97/21725; *Chem. Abst.* **1997**, *127*, 122002. (f) Aeruginosin 103A: Kodani, S.; Ishida, K.; Murakami, M. *J. Nat. Prod.* **1998**, *61*, 1046. (g) Microcin SF608: Banker, R.; Carmelli, S. *Tetrahedron* **1999**, *55*, 10835. (h) Aeruginosins 98C, 101, 298B, 89A, and 89B: Ishida, K.; Okita, Y.; Matsuda, H.; Okino, T.; Murakami, M. *Tetrahedron* **1999**, *55*, 10971. (i) Aeruginosin EI461: Pluotno, A.; Shoshan, M.; Carmelli, S. *J. Nat. Prod.* **2002**, *65*, 973.
- (7) (a) Dysinosin A: Carroll, A. R.; Pierens, G.; Fechner, G.; de Almeida Leone, P.; Ngo, A.; Simpson, M.; Hooper, J. N. A.; Boström, S.-L.; Musil, D.; Quinn, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 13340. (b) Chlorodysinosin A: Goetz, G. H.; Harrigan, G. G.; Likos, J. J.; Kasten, T. P. PCT WO03/051831; *Chem. Abst.* **2003**, *139*, 47155. (c) Dysinosins B, C, and D: Carroll, A. R.; Buchanan, M. S.; Edser, A.; Hyde, E.; Simpson, M.; Quinn, R. J. *J. Nat. Prod.* **2004**, *67*, 1291.
- (8) Total syntheses of aeruginosins 298A: (a) Methot, J.-L.; Wipf, P. *Org. Lett.* **2000**, *2*, 4213. (b) Valls, N.; López-Canet, M.; Vallribera, M.; Bonjoch, J. *J. Am. Chem. Soc.* **2000**, *122*, 11248. (c) Ohshima, T.; Gnanadesikan, V.; Shibuguchi, T.; Fukuta, Y.; Nemoto, T.; Shibasaki, M. *J. Am. Chem. Soc.* **2003**, *125*, 11206. (d) For the total synthesis of aeruginosins 298B, see: Valls, N.; López-Canet, M.; Vallribera, M.; Bonjoch, J. *Chem.—Eur. J.* **2001**, *7*, 3446.
- (9) Aeruginosin EI461: Valls, N.; Vallribera, M.; Carmeli, S.; Bonjoch, J. *Org. Lett.* **2003**, *5*, 447.
- (10) Microcin SF608: Valls, N.; Vallribera, M.; López-Canet, M.; Bonjoch, J. *J. Org. Chem.* **2002**, *67*, 4945.
- (11) Oscillarin: Hanessian, S.; Tremblay, M.; Petersen, J. F. W. *J. Am. Chem. Soc.* **2004**, *126*, 6064.
- (12) Dysinosin A: Hanessian, S.; Margarita, R.; Hall, A.; Johnstone, S.; Tremblay, M.; Parlanti, L. *J. Am. Chem. Soc.* **2002**, *124*, 13342.
- (13) The originally proposed structures of aeruginosins 298A, 298B, EI461 and oscillarin have been revised through synthesis. The proposed structures of aeruginosins 205A and 205B have been called into question through synthesis and NMR analysis of the putative hydroindole core residue (see ref 14a).
- (14) (a) For a stereoselective synthesis of diastereomeric 3-chloroleucines, see: Valls, N.; Borregán, M.; Bonjoch, J. *Tetrahedron Lett.* **2006**, *47*, 3701. (b) A nondiastereoselective synthesis of racemic 3-chloroleucine has been reported: Hayashi, K.; Skinner, C. G.; Shive, W. J. *Org. Chem.* **1961**, *26*, 1167.
- (15) (a) For an insightful report on the possible link between metabolites from *Oscillatoria* cyanobacteria and *Lamellosidea* marine sponges, see: Ridley, C. P.; Bergquist, P. R.; Harper, M. K.; Faulkner, D. J.; Hooper, J. N. A.; Haygood, M. G. *Chem. Biol.* **2005**, *12*, 397. (b) Vaillancourt, F.; Yeh, E.; Vosburg, D. A.; Garneau-Tsodikova, S.; Walsh, C. T. *Chem. Rev.* **2006**, ASAP. (c) van Peé, K.-H. *Annu. Rev. Microbiol.* **1996**, *50*, 375. (d) Gribble, G. J. *Nat. Prod.* **1992**, *55*, 1353. (e) Bewley, C. A.; Faulkner, D. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 2162. (f) Fusetani, N.; Matsunaga, S. *Chem. Rev.* **1993**, *93*, 1783. (g) Fukuchi, N.; Isogai, A.; Yamashita, S.; Suyama, K.; Takemoto, J. Y.; Suzuki, A. *Tetrahedron Lett.* **1990**, *31*, 1589. (h) Moore, R. E.; Bornemann, V.; Niemczura, W. P.; Gregson, J. M.; Chen, J.-L.; Norton, T. R.; Patterson, G. M. L.; Helms, G. L. *J. Am. Chem. Soc.* **1989**, *111*, 6128.
- (16) (a) Morita, H.; Nagashima, S.; Koichi, T.; Itokawa, H. *Chem. Pharm. Bull.* **1993**, *41*, 992. For examples of other peptide natural products featuring β -chlorinated proline residues, see: (b) Marumo, S.; Sumiki, Y. *Nippon Nogei Kagaku Kaishi* **1955**, *29*, 395. (c) Ghosh, A. C.; Ramgopal, M. J. *Heterocycl. Chem.* **1980**, *17*, 1809. (d) Kosemura, S.; Ogawa, T.; Kazuo, T. *Tetrahedron Lett.* **1993**, *34*, 1291.
- (17) (a) Kuroda, Y.; Okuhara, M.; Goto, T.; Yamashita, M.; Iguchi, E.; Kohsaka, M.; Aoki, H.; Imamura, H. *J. Antibiot.* **1980**, *33*, 259. (b) Yasuda, N.; Sakane, K. *J. Antibiot.* **1991**, *44*, 801.
- (18) Ohtsu, Y.; Sasamura, H.; Tsurumi, Y.; Yoshimura, S.; Shigematsu, N.; Takase, S.; Hashimoto, M.; Shibata, T.; Hino, M.; Fujii, T. *J. Antibiot.* **2003**, *56*, 682.
- (19) For reviews on the synthesis of fluorinated amino acids, see: (a) Kukhar, V. P.; Soloshonok, V. A. *Fluorine Containing Amino Acids: Synthesis and Properties*; Wiley: New York, 1995. (b) Qiu, X.-L.; Meng, W.-D.; Qing, F.-L. *Tetrahedron* **2004**, *60*, 6711. (c) Sutherland, A.; Willis, C. L. *Nat. Prod. Rep.* **2000**, *17*, 621. For relevant examples of the synthesis of other halogenated amino acids, see: (d) Meyer, F.; Laaziri, A.; Papini, A. M.; Uziel, J.; Jugé, S. *Tetrahedron: Asymmetry* **2003**, *14*, 2229. (e)

- Pansare, S. V.; Vederas, J. C. *J. Org. Chem.* **1989**, *54*, 2311. (f) Chuang, T.-H.; Sharpless, K. B. *Org. Lett.* **2000**, *2*, 3555. (g) Choi, D.; Kohn, H. *Tetrahedron Lett.* **1995**, *36*, 7011. (h) Righi, G.; D'Achille, R. *Tetrahedron Lett.* **1996**, *37*, 6893. (i) Schumacher, K. K.; Jiang, J.; Joullié, M. M. *Tetrahedron: Asymmetry* **1998**, *9*, 47. (j) Laszlo, S. E.; Willard, P. G. *J. Am. Chem. Soc.* **1985**, *107*, 199.
- (20) (a) Srinivasan, A.; Stephenson, R. W.; Olsen, R. K. *J. Org. Chem.* **1977**, *42*, 2253. (b) Dunn, M. J.; Gomez, S.; Jackson, R. F. W. *J. Chem. Soc., Perkin Trans. I* **1995**, 1639. (c) Gelb, M. H.; Lin, Y.; Pickard, M. A.; Song, Y.; Vederas, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 4932. (d) Murkin, A. S.; Tanner, M. E. *J. Org. Chem.* **2002**, *67*, 8389.
- (21) For the opening of *N*-Boc aziridines with MgBr₂ and MgBr₂/NaI as halide sources, see: (a) Righi, G.; Franchini, T.; Bonini, C. *Tetrahedron Lett.* **1998**, *39*, 2385. For recent reviews on halogenolysis of activated aziridines, see: (b) Righi, G.; Bonini, C. *Recent Res. Org. Chem.* **1999**, *343*. (c) McCoull, W.; Davis, F. A. *Synthesis* **2000**, 1347. (d) Hu, X. E. *Tetrahedron* **2004**, *60*, 2701.
- (22) Caldwell, C. G.; Bondy, S. S. *Synthesis* **1990**, 34.
- (23) Sabitha, G.; Babu, R. S.; Rajkumar, M.; Reddy, Ch. S.; Yadav, J. S. *Tetrahedron Lett.* **2001**, *42*, 3955.
- (24) Sun, P.; Weinreb, S. J. *Org. Chem.* **1997**, *62*, 8604.
- (25) Gontcharov, A. V.; Liu, H.; Sharpless, K. B. *Org. Lett.* **1999**, *1*, 783.
- (26) Zhao, M.; Li, J.; Song, Z.; Desmond, R.; Tschaen, D. M.; Grabowski, E. J. J.; Reider, P. J. *Tetrahedron Lett.* **1998**, *39*, 5323.
- (27) For a review of peptide coupling methods as applied to the synthesis of complex natural products, see: Humphrey, J. M.; Chamberlin, A. R. *Chem. Rev.* **1997**, *97*, 2243.
- (28) (a) Li, H.-T.; Jiang, X.-H.; Ye, Y.-H.; Fan, C.-X.; Romoff, T.; Goodman, M. *Org. Lett.* **1999**, *1*, 91. (b) Fan, C.-X.; Hao, X.-L.; Ye, Y.-H. *Synth. Commun.* **1996**, *26*, 1455. For discussions on the effectiveness of DEPBT in difficult coupling reactions en route to complex natural products, see: (c) Jiang, W.; Wanner, J.; Lee, R. J.; Bounaud, P.-Y.; Boger, D. L. *J. Am. Chem. Soc.* **2003**, *125*, 1877. (d) Ye, Y.-H.; Li, H.-T.; Jiang, X.-H. *Biopolymers* **2005**, *80*, 172.
- (29) See: Hanessian, S.; Kagotani, M. *Carbohydr. Res.* **1990**, *202*, 67 and referenced cited therein.
- (30) Ohno, M.; Otsuka, M. *Org. React.* **1989**, *37*, 1.
- (31) (a) Reddy, L. R.; Fournier, J.-F.; Reddy, B. V. S.; Corey, E. J. *J. Am. Chem. Soc.* **2005**, *125*, 8974. (b) Reddy, B. V. S.; Rajender, Reddy, L. J.; Corey, E. J. *Tetrahedron Lett.* **2005**, *46*, 4589.
- (32) For a recent application, see: (a) Nicolaou, K. C.; Estrada, A. A.; Zak, M.; Lee, S. H.; Safina, B. S. *Angew. Chem., Int. Ed.* **2005**, *44*, 1378. See also: (b) David, S.; Hanessian, S. *Tetrahedron* **1985**, *4*, 643.
- (33) (a) Lubineau, A.; Lemoine, R. *Tetrahedron Lett.* **1994**, *35*, 8795. (b) Sanders, W. J.; Manning, D. D.; Koeller, K. M.; Keissling, L. L. *Tetrahedron* **1997**, *53*, 16391.
- (34) Nilsson, T.; Sjoling-Ericksson, A.; Deinum, J. *J. Enzyme Inhibition* **1998**, *13*, 11.
- (35) Data for cocrystal structure of **2** bound to thrombin has been registered with the protein data bank under PDB ID: 2GDE.
- (36) (a) Recacha, R.; Costanzo, M. J.; Maryanoff, B. E.; Carson, M.; DeLucas, L.; Chattopadhyay, D. *Acta Crystallogr.* **2000**, *D56*, 1395. (b) Malikowski, M. G.; Martin, P. D.; Guzik, J. C.; Edwards, B. F. P. *Protein Sci.* **1997**, *6*, 1438.
- (37) See Supporting Information for experimental details on molecular modeling and for a comparison of χ^1 angles and energy minimized conformations of **1** and **2**.
- (38) Ward, W. H; Holdgate, G. A. *Prog. Med. Chem.* **2001**, *38*, 309.

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