S1. Cyanobacterial Collection and General Experimental Procedures for Wewakazole (1)

Cyanobacterial Collection. The marine cyanobacterium *Lyngbya majuscula* (Dillwyn) Harvey (Oscillatoriaceae) (voucher specimen available as collection number PNSB-5/Sept/98-02) was collected by B. Marquez, W. Gerwick and S. Ketchum in Wewak Bay, Papua New Guinea, on September 5, 1998. The material was stored in 2-propanol at -20 °C until extraction.

General Experimental Procedures. Optical rotations were measured on a Perkin-Elmer 243 polarimeter. IR and UV spectra were recorded on Nicolet 510 and Beckman DU640B spectrophotometers, respectively. All NMR spectra were recorded on Bruker DRX600 and AM400 spectrometers with the solvent CDCl₃ used as an internal standard (δ 77.23, J 7.27). Chemical shifts are reported in ppm and coupling constants (J) are reported in Hz. FABMS and MS/MS data were recorded on Kratos MS50TC and Perkin-Elmer Sciex API3 mass spectrometers, respectively. HPLC isolations were performed using a Waters Millipore Lambda-Max model 480 LC spectrophotometer with Waters 515 HPLC pumps.

Stereochemical Analysis of Wewakazole (1). A stream of ozone was bubbled through approximately 1.0 mg of 5 dissolved in 2 mL of CH₂Cl₂ at -78 °C until the solution turned pale blue (ca. 1 min). The solvent was removed under a stream of N₂, and the sample was hydrolyzed with 6N HCl at 110 °C for 14 h. A portion of the hydrolysate was evaporated to dryness and resuspended in H₂O (100 L). A 0.1% 1-fluoro-2,4-dinitrophenyl-5-L-alaninamide solution in acetone (L-Marfey's reagent, 20 L) and 1N NaHCO₃ (10 L) were added to the hydrolysate, and the mixture was heated at 40 °C for 1 h. The solution was cooled to room temperature, neutralized with 2N HCl (5 L) and dried. The residue was resuspended in 1:1 DMSO/H₂O (50 L) and analyzed by reversed-phase HPLC [LiChrospher 100 C₁₈, 5 µ 125 mm, UV detection at 340 nm] using a linear gradient of 9:1 50 mM triethylamine phosphate (TEAP) buffer to 1:1 TEAP/CH₃CN over 60 min.

The retention times (tᵣ, min) of the derivatized residues in the hydrolysate of I matched L-Ala (19.7; D-Ala, 21.2), L-Val (28.4; D-Val, 33.9), and L-Phe (36.7; D-Phe, 40.1). However, the retention times for the L-Ile and L-allo-Ile standards (34.3) were identical, as were the retention times for the D-Ile and D-allo-Ile standards (35.8). Thus, we could only conclude that the isoleucine residue of I was either of L- or L-allo- configuration. Additionally, though Marfey analysis of the hydrolysate indicated the presence of at least one L-Pro residue (22.2), the underivatized Marfey reagent eluted simultaneously with the D-Pro standard (25.4), precluding the stereochemical analysis of the three proline residues of I by this method.

The second portion of the hydrolysate was also dried under N₂ and 100 L of a 1:5 acetyl chloride/2-propanol mixture was added. The solution was heated to 105 °C for 45 min, dried under N₂ and resuspended in 200 L of CH₂Cl₂. Approximately 100 L of pentafluoropropanoic anhydride (PFPA) were added, and the solution was heated to 105 °C for 15 min. After drying under N₂, the derivatized hydrolysate was resuspended in CH₂Cl₂ and analyzed by capillary GC-MS (Alltech Chiralsil-Val 25 m × 0.25 mm column, oven temperature held at 70 °C for 0.5 min after injection of the sample, then increased from 70 °C to 180 °C at a rate of 4 °C/min). The tᵣ (min) of derivatized residues in the wewakazole hydrolysate confirmed an L-configuration for the L-Ala (5.1; D-Ala, 4.5), L-Val (6.5; D-Val, 6.1), and L-Phe (19.5; D-Phe, 19.2) residues of I. Additionally, the Ile residue was also determined to be of an L-configuration (tᵣ 8.3, L-allo-Ile, 8.0). Chiral GC-MS analysis, using a temperature ramp of 0.5 °C/min, clearly demonstrated that all three proline residues of wewakazole were also of L-stereochemistry (L-Pro, 25.7 and D-Pro, 25.3 min).
S2. 400 MHz $^1$H NMR spectrum and 100 MHz $^{13}$C NMR spectrum of wewakazole (1) in CDCl$_3$. 
S3. 400 MHz HSQC spectrum of weakazole (I) in CDCl₃.
S4. 400 MHz TOCSY spectrum of wewakazole (1) in CDCl₃.
S5. 400 MHz HMBC spectrum (optimized for 8 Hz coupling) of wewakazole (1) with expansion of the oxazole methine signals.
S6. Illustration of some key MS/MS fragmentation ions supporting the amino acid sequencing in wewakazole (1).
S7. Pulse sequence for the 1D HMBC sequence utilized in this structure determination. Narrow and thick bars represent 90 degree and 180 degree pulses, respectively. The delay is the delay for the evolution of long-range heteronuclear coupling (1/2J). The S₁ pulse is a ¹³C selective pulse. The basic phase cycle is \( y, x; R = y, x \). The gradient ratios are set to 50:-30 and are of 1 ms duration.