SUPPLEMENTARY INFORMATION

Boron Binding with the Quorum Sensing Signal AI2 and Analogs

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Borate Binding Studies by ^{11}B NMR Spectroscopy.

The majority of the ^{11}B NMR spectra were collected at 20 °C using a Varian Unity/INOVA spectrometer at 160.5 MHz equipped with a 5-mm tunable X/^{1}H probe (Nalorac), and were referenced indirectly to $BF_3O(Et)_2$. For D-ribose, a Varian Unity/INOVA spectrometer at 128.4 MHz equipped with a 8-mm tunable X/^{1}H probe (Nalorac) was used. A collection of 128 scans was averaged for each spectrum with a 0.25-s recycle time using an approximately 30° flip-angle pulse. Determination of relative boron binding affinities was performed by ^{11}B NMR by placing 5 mg of each compound into 0.5 mL of D_2O saturated with $B(OH)_3$ and $NaHCO_3$ (pH 7.8). Spectra used for chemical shift references (1,2-cyclopentanediol and D-ribose) were collected as above except that 1.0 mL of solvent and 20 mg of compound were used.

Titration of Laurencione (5) into Borate Monitored by ^{11}B NMR.

The ^{11}B NMR spectra were collected at 20 °C using a Varian Unity/INOVA spectrometer at 160.5 MHz equipped with a 5-mm tunable X/^{1}H probe (Nalorac), and were referenced indirectly to $BF_3O(Et)_2$. A mixture of laurencione with 1,4-dioxane (7:3 mol ratio) was used to lower the viscosity of the laurencione for ease of transfer. Aliquots (increments increased from 3 μL to 35 μL over the course of the titration) of the laurencione mixture were then added to an NMR tube (5-mm) containing 1.0 mL of sat. $B(OH)_3$ and sat $NaHCO_3$ in D_2O (pH 7.8). Addition of laurencione was continued until a change in the intensity of the $B(OH)_3$ peak was undetectable.

Boronate Affinity Column Capture-and-Release Procedure for DPD.

An aliquot of resuspended immobilized boronic acid gel (200 μL suspension, polyacrylamide spherical beads, *m*-aminophenyl spacer, 100 μmoles boronate/mL of gel loading) was placed in a microcentifuge filter (10,000 MW cutoff, 500 μL volume) and centrifuged (9000 rpm) to dry the polymer. The dried polymer was then washed twice with 250 μL sat $NaHCO_3$ prior to treatment with DPD. The crude enzymatic preparation of DPD was then added to the dried polymer in 350μL aliquots, and the suspension was centrifuged until dry. After the entirety of the crude DPD had been passed over the beads, 200 μL sat. $NaHCO_3$ was used to wash the polymer. At this time the DPD was released from the polymer by adding 2 x 250 μL aliquots of 10-20% formic acid to the polymer, and the eluant containing released DPD was collected in a 1.5-mL microcentrifuge tube containing ~25 mg of sat. $NaHCO_3$ and ~10 mg of $B(OH)_3$. The addition of the $NaHCO_3$ to the tube insured that the pH of the solution containing the released DPD was buffered in order to minimize decomposition of the molecule. Note, the beads loaded with DPD could be stored at -20 °C for at least three days with no detectable loss in activity (as monitored by the *V. harveyi* bioassay upon release from the polymer).

Bioassay Procedure. [Adapted by: Schauder, S. *et. al., Mol. Microbiol.* 2001, *41*, 463-476.]
Vibrio harveyi strain MM32 (*luxN*$^-$ *luxS*$^-$) cells were grown overnight then diluted 5,000-fold in AB growth medium. To 90 ul of diluted cells, 10 ul of a compound was added, and this culture was grown in a 96-well microtiter dish at 30 ^{o}C for approximately 6 h. The concentration of crude DPD was calculated by measuring the amount of homocysteine released in an Ellman's test. Light emission was measured using a Wallac model 1450 microbeta Plus scintillation counter.

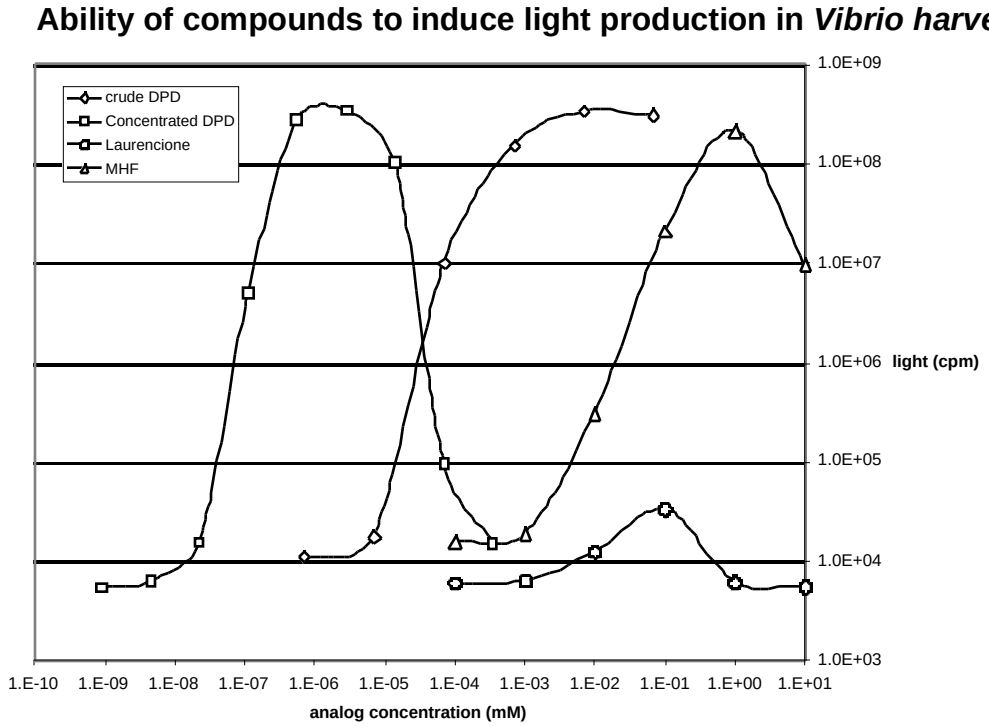

Figure 1. Titration curves for tested analogs using *Vibrio harveyi* reporter strain (*luxN*$^-$ *luxS*$^-$). Light production by *V. harveyi* was measured over several concentrations for each analog. The "concentrated DPD" curve is the eluant from the affinity column while "crude DPD" refers to the broth from the biosynthesis preparation. Diamonds, crude DPD; squares, concentrated DPD; circles, laurencione; triangles, MHF. Note: the activity is measured by the concentration at which light emission is initiated, not the absolute magnitude of light production.

Mass Spectral Analysis
Mass spectral analyses were performed using a Hewlett Packard 5989B MS Engine fitted with an electrospray source. Compounds were dissolved in sat. aq. $NaHCO_3$ (aq) and sat. $B(OH)_3$ (aq) and then diluted with H_2O (pH adjusted to 9 by addition of NH_4OH) prior to analysis.