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HYELLAZOLE AND CHLOROHYELLAZOLE, TWO NOVEL CARBAZOLES FROM THE BLUE-GREEN ALGA HYELLA CAESPITOSA BORN. ET FLAH.

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Summary. The structures of two carbazoles, hyellazole and 6-chlorohyellazole, from the blue-green alga *Hyella caespitosa* are reported. The structure of 6-chlorohyellazole was solved by X-ray crystallographic methods.

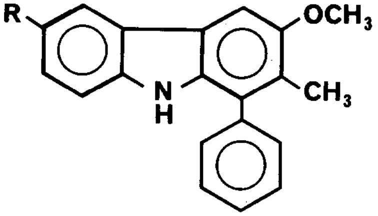
Alkaloids are present in blue-green algae. Lyngbyatoxin A, a potent inflammatory agent from a shallow-water variety of the cyanophyte *Lyngbya majuscula*, represents the first basic indole alkaloid to be isolated from a marine plant.[1] We report here the isolation of two unusual non-basic carbazole alkaloids, hyellazole (**1**) and 6-chlorohyellazole (**2**), from a supralittoral variety of the blue-green alga *Hyella caespitosa*.[2] The hyellazoles possess structures that are entirely different from carbazole alkaloids of terrestrial plants.[3]

The alga was collected from a path leading from the Cable Station to the lagoon of Fanning Island. The MeOH extract was distributed between H_2O and EtOAc and the material in the EtOAc phase was then partitioned between CCl_4 and 75% MeOH-H_2O. Further separation of the oil in the CCl_4 layer was achieved by gel filtration on Sephadex LH-20 (1:1 $CHCl_3$-MeOH) and LC on μ-Bondapak C-18 (3:2 CH_3CN-H_2O) to give **1**, mp 133-134° (0.012% dry alga) and **2**, mp 163-164° (0.009%).

The high resolution MS indicated molecular formulae $C_{20}H_{17}NO$ for **1** and $C_{20}H_{16}C\ell NO$ for **2**. The ^1H and ^{13}C-NMR spectra established that **1** and **2** had OCH_3 and $ArCH_3$ groups and the UV spectra suggested that **1** and **2** were carbazoles.[4,5] The IR band at 3490 cm^{-1} for **1** had to be due to NH. The ^1H-NMR spectrum of **1** showed a signal pattern that was typical for an unsubstituted benzenoid ring of a carbazole system,[6] but the ^1H-NMR spectrum of **2** indicated that the chlorine was on this ring para to the NH.[7] The remaining signals in the two spectra were essentially superimposable and this meant that the substitution on the other benzenoid ring of the carbazole had to be identical for both **1** and **2**.

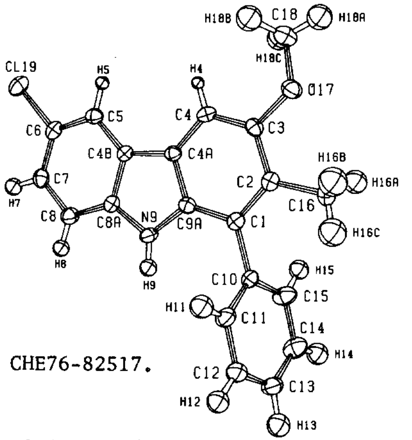
The substitution pattern was solved by X-ray analysis of **2**. A single crystal of **2**, with dimensions 0.23 × 0.17 × 0.16 mm, was mounted on a Syntex $P\bar{1}$ diffractometer. Monochromatized Mo $K\alpha$ radiation ($K\alpha_1$, $\lambda = 0.70930$ Å; $K\alpha_2$, $\lambda = 0.71359$ Å) was used. The θ-2θ scanning mode was used with a constant scan rate in 2θ of 2° min^{-1}. Of the 2124 unique reflections measured ($3° < 2\theta < 45°$), 1443 had intensities such that $I > 2\sigma(I)$. Corrections for Lorentz and polarization effects,[8a] but not for absorption ($\mu = 2.4$ cm^{-1}), were made. An overall thermal parameter of 5.0 $Å^2$ and normalized structure factor amplitudes for the 250 reflections with $|E| \geq 1.57$ were used in the program MULTAN.[8b] A three-dimensional E function, phased as indicated by the solution with the largest CFOM, 2.54, revealed all nonhydrogen atoms. After several cycles of fullmatrix least-squares refinement ^{8c} of the 23 nonhydrogens, all 16 hydrogens were located on a Fourier difference synthesis. Finally, several cycles of least-squares refinement with anisotropic thermal parameters for the nonhydrogens and isotropic thermal parameters for the hydrogens led to the final error indices R_1 = 0.047 and R_2 = 0.039. The overdetermination ratio is 5.3. Crystal Data: $C_{20}H_{16}ClNO$, monoclinic, $P2_1/c$, a = 10.124(2) Å, b = 11.293(3) Å, c = 14.206(6) Å, β = 94.06(3)°, V = 1620(1) Å^3, d_{calcd} = 1.319 g cm^{-3}, Z = 4, MW = 321.8.

The carbazole ring system of **2** is quite planar; the maximum deviation from the least-squares plane is -0.04 Å at C(1). The large angle between the carbazole and phenyl planes, 73.9°, is a result of steric repulsions: H(11)···H(9) = 3.07 Å and H(15)···H(16C) = 3.02 Å.



1 R = H

2 R = Cl



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2. T. V. Desikachary, "Cyanophyta," Indian Council of Agricultural Research, New Delhi, 1959, p. 183. The alga was identified by Dr. Dennis Russell, Department of Botany, University of Hawaii. A voucher specimen of the alga has been retained.
3. D. P. Chakraborty, Fortschr. Chem. Organ. Naturstoffe, **34**, 299 (1977).
4. Spectral data for **1**: UV (EtOH) λ_{max} sh 226 nm (ε 34,000), 232 (36,500), sh 238 (34,500), sh 250 (20,000), sh 260 (13,500), sh 292 (12,500), 304 (18,500), 338 (4500), 352 (5000) -- unchanged on the addition of acid or base; IR (CCl_4) ν_{max} 3490 cm^{-1}; ^{1}H NMR (acetone-d_6, δ 2.05) δ 9.52 (br s, NH), 8.08 (br d, J = 8 Hz, H on C-5), 7.70 (s, H on C-4), 7.6-7.35 (m, 6H with H on C-8 at ∿ 7.5 from decoupling experiments), 7.28 (dt, J = 7.5 and 1 Hz, H on C-7), 7.11 (dt, J = 7 and 1 Hz, H on C-6), 3.99 (s, OCH_3), 2.14 (s, C-CH_3); ^{13}C NMR ($CDCl_3$, δ 76.9) δ 152.5 (s), 139.3 (s), 137.3 (s), 133.1 (s), 129.7 (d, 2CH), 128.8 (d, 2CH), 127.4 (d), 125.4 (s), 124.9 (d), 123.7 (s), 123.5 (s), 120.2 (s), 119.7 (d), 118.7 (d), 110.5 (d), 100.2 (d), 56.1 (q, OCH_3), 13.7 (q); HRMS m/e 287.130 (M^+).
5. Spectral data for **2**: UV (EtOH) λ_{max} 220 nm (ε 32,600), 235 (32,600), 242 (32,700), sh 255 (20,000), sh 272 (14,600), sh 300 (13,200), 310 (18,000), 348 (4400), 360 (4200); ^{1}H NMR (acetone-d_6) δ 9.70 (br s, NH), 8.13 (d, J = 2 Hz, H on C-5), 7.75 (br s, H on C-4), 7.6-7.35 (m, 6H with H on C-8 at ∿ 7.5), 7.27 (dd, J = 8.5 and 2 Hz, H on C-7), 3.99 (s, OCH_3), 2.14 (s, C-CH_3); ^{13}C NMR ($CDCl_3$) δ 152.6 (s), 137.5 (s), 136.8 (s), 133.6 (s), 129.5 (d, 2CH), 128.9 (d, 2CH), 127.5 (d), 125.5 (s), 125.3 (s), 124.5 (d), 124.0 (s, 2C), 119.5 (s), 119.3 (d), 111.4 (d), 99.9 (d), 56.1 (q, OCH_3), 13.7 (q); HRMS m/e 321.090 (M^+).
6. F. Balkau and M. L. Heffernan, Aust. J. Chem., **26**, 1501 (1973).
7. The δ and J values are identical to those of a synthetic sample of 3-chlorocarbazole.
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