(3 H, s, C-16), 1.67 (3 H, s, C-17), 1.65 (1 H, m, C-2), 1.61 (3 H, m, C-3, C-6), 1.45 (1 H, m, C-5), 1.25 (3 H, d, J = 6.9 Hz, C-19), 1.14 (1 H, m, C-5), 1.04 (3 H, d, J = 5.9 Hz, C-18).

Acid Hydrolysis of Pseudopterosin A (1). Conditions for reaction of 1 with 1 N HCl, which allowed the sugar residue to be isolated, were first worked out with D- and L-xylose alone. If the concentration of HCl was much greater than 1 N, the temperature of the reaction was above 50 °C, and/or if the H_2O was totally removed in the vacuum desiccator prior to measuring the optical rotations, either the values of the rotations were irreproducible or no optical rotation could be measured at all. Pseudopterosin A (1; 63.0 mg, 0.146 mmol) was treated with 1 N HCl by the same procedure outlined above for the acid hydrolysis of **3** and **9**, except that the volume was doubled and the workup was slightly modified. After 3 h, 4.0 mL of water was added, the MeOH was removed by evaporation with a N_2 stream, and the remaining aqueous solution was then repeatedly extracted with EtOAc (3 × 20 mL), until all color was extracted from the aqeous layer. Both the aqueous solution and the combined EtOAc layers were saved. The combined EtOAc layers were washed with $NaHCO_3$ (3 × 20 mL), dried ($MgSO_4$), filtered, and evaporated to yield 39.8 mg (91% from **1**) of the *o*-quinone **7**. Next, any remaining EtOAc was removed from the aqueous layer with a stream of N_2. This solution was then transferred to a small beaker: the HCl was removed, and the H_2O was reduced to a volume slightly less than 1.5 mL in a vacuum desiccator that contained pellets of NaOH. Once the volume was reduced below 1.5 mL (in approximately 48 h), water was added to bring the volume to 2.0 mL. This solution, containing the sugar residue of **1**, showed $[\alpha]^{20}_D$ +29° (*c* 0.95, H_2O). Simutaneously, as controls and for comparison, samples of the pentose sugars D-xylose (32.0 mg) and L-xylose (30.8 mg) (Aldrich Chemical Co.) were also treated with 1 N HCl. Upon completion of the reaction, the acid was removed and the aqueous solution reduced in the same manner as described above. After treatment with 1 N HCl, D-xylose showed $[\alpha]^{20}_D$ +23° (*c* 1.64, H_2O) and L-xylose showed $[\alpha]^{20}_D$ −26° (*c* 1.54, H_2O).

Single-Crystal X-ray Structure Determination of Pseudopterosin C. Preliminary X-ray photographs displayed monoclinic symmetry, and accurate lattice constants of a = 10.177 (1) Å, b = 9.992 (1) Å, c = 17.757 (1) Å, and β = 68.00 (3)° were determined from a least-squares fit of 15 diffractometer measured 2θ values between 35 and 50° [Cu K$\bar{\alpha}$ radiation (1.541 78 Å)]. The presence of chirality, systematic extinctions, and crystal density were uniquely accommodated by space group $P2_1$, with 1 molecule of $C_{26}H_{38}O_5$ forming the asymmetric unit. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a computer-controlled four-circle diffractometer using graphite-monochromated Cu K$\bar{\alpha}$ radiation (1.541 78 Å) and variable-speed, 1° ω-scans. A total of 2012 reflections were measured in this fashion, and, after correction for Lorentz, polarization, and background effects, 1799 (89%) were judged observed [$|F_o| \geq 3\sigma(F_o)$].[14] A phasing model was found using 300 normalized structure factors in a multisolution tangent formula approach. The use of the negative quartets figure of merit was decisive in finding the best phase set. The E-synthesis from the best set showed 19 plausible atoms, and this was extended to 24 atoms by tangent formula recycling.[15] The structure was completed by Fourier refinement with $2F_o-F_c$ syntheses. Block-diagonal least-squares refinements with anisotropic non-hydrogen atoms have converged to the present residual of 0.09 for the observed data. Additional crystallographic details are available and are described (supplementary material).

Acknowledgment. Research at the Scripps Institution of Oceanography was supported in part by the National Science Foundation, Chemistry Division, under Grants CHE81-11907 and CHE83-15546. We appreciate the ship support funding, also provided by NSF, which enabled us to utilize the University of Miami's Research Vessel CALANUS. The pharmacological development of these compounds was the result of financial support from NOAA, National Sea Grant Program, through Project R/MP-32 of the California Sea Grant Program. The Cornell investigators acknowledge financial support from the NIH (Grant CA 24487) and the New York Sea Grant Program.

Supplementary Material Available: Tables of fractional coordinates, bond distances, bond angles, and torsion angles for pseudoterosin C (6 pages); tables of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Annulins A and B, Metabolites of the Marine Hydroid *Garveia annulata*

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Two new antimicrobial metabolites have been isolated from the marine hydroid *Garveia annulata*. The structure of annulin A (**3**) was determined via X-ray diffraction analysis, and the proposed structure for annulin B (**4**) was inferred from its spectral data.

We have recently shown that the marine hydroid *Garveia annulata* is a rich source of antimicrobial 1-(4*H*)-anthracenone derivatives.[1,2] Garveatin A (**1**) and 2-hydroxygarvin A (**2**) are representative members of the garveatin and garvin families, which encompass all the *Garveia* metabolites described to date. We now report the isolation of two degraded anthracenes, annulins A (**3**) and B (**4**), from *G. annulata* methanol extracts.

G. annulata was collected by hand using SCUBA in Barkley Sound, British Columbia, and its metabolites were extracted and purified as previously described.[2]

Annulin A (**3**), obtained from ethanol as optically inactive bright orange crystals (mp 174–176 °C), showed a parent ion in the HREIMS that was consistent with a molecular formula of $C_{19}H_{20}O_7$ (M^+ 360.1221, calcd 360.1209). The ^1H NMR spectrum of annulin A contained resonances that could be assigned to aromatic methyl (2.44

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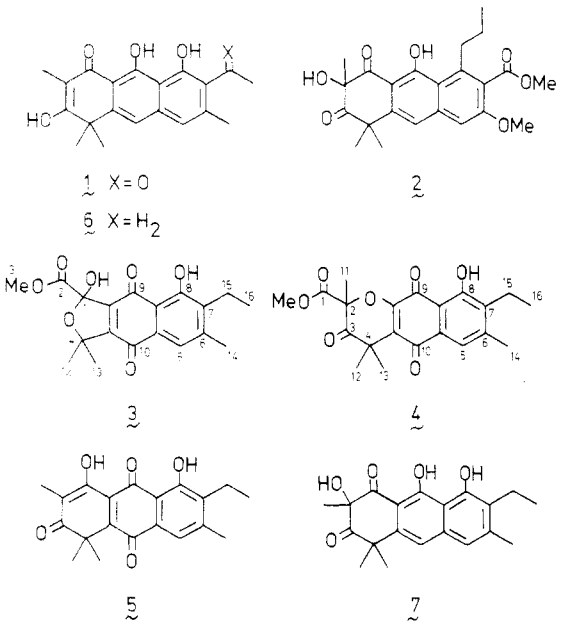
0022-3263/86/1951-5145$01.50/0

Chart I



1 X=O
6 X=H_2
2
3
4
5
7

Table I. ^{1}H NMR (300 MHz, $CDCl_3$) Data (Chemical Shifts in ppm from Me_4Si)

proton on C no.	annulin A (3)	annulin B (4)	garveatin B quinone (5)
1-OH	4.92 s		11.79 s
3	3.87 s		
5	7.47 s	7.31 s	7.51 s
8-OH	12.12 s	12.35 s	11.84 s
11		1.85 s	1.97 s
12	1.63 s[a]	1.49 s[a]	1.61 s
13	1.72 s[a]	1.51 s[a]	1.61 s
14	2.44 s	2.42 s	2.45 s
15	2.76 q	2.73 q	2.78 q
16	1.14 t	1.15 t	1.16 t
17		3.76 s	

[a] Assignments may be reversed.

ppm, q, 2 H), and ethyl (1.14 ppm, t, 3 H; 2.76 ppm, q, 2 H) substituents, a methyl ether or ester (3.87 ppm, s, 3 H), and two aliphatic methyl groups (1.63 ppm, s, 3 H; 1.72 ppm, s, 3 H). Subtracting the six carbon atoms required by the methyl and ethyl resonances observed in the ^{1}H NMR of annulin A from its molecular formula leaves a residue of 13 carbons, indicating that the 14-carbon anthracene-type skeleton of the previously reported *Garveia* metabolites could not be present.

Additional resonances in the ^{1}H NMR spectrum of annulin A could be assigned to a single aromatic proton (7.47 ppm, s, 1 H) and a phenolic proton (12.12 ppm, s, 1 H). The chemical shifts of the resonances assigned to the aromatic proton, the phenolic proton, and the aromatic methyl and ethyl groups bore a striking resemblance to the chemical shifts of the corresponding resonances in the ^{1}H NMR spectrum of garveatin B quinone (**5**), an artifact formed during silica gel purification of garveatin B (**6**) (Table I).[2] This similarity suggested that annulin A contained a napthoquinone nucleus with substituents on the aromatic ring identical with those present in garveatin B quinone (**5**). Consistent with this assignment was the observation of H-bonded (1616-cm^{-1}) and non-H-bonded (1657-cm^{-1}) quinone carbonyl stretching bands in the IR spectrum, a base-induced bathochromic shift to 559 nm characteristic of napthoquinones in the UV/visible spectrum, and two carbonyl resonances at 180.91 and 185.97

Table II. ^{13}C NMR (75 MHz, $CDCl_3$) Data (Chemical Shifts in ppm from Me_4Si)

C no.	annulin A (3)	annulin B (4)	C no.	annulin A (3)	annulin B (4)
1	101.45	167.68	9a	140.76[a]	163.79
2	169.35	84.48	10	180.91	178.62
3	54.04	203.02	10a	130.37	127.59
4	89.08	43.64	11		20.38
4a	154.29	119.11	12	26.43[a]	23.78[a]
5	122.10	120.65	13	27.94[a]	25.90[a]
6	145.63	147.64	14	20.08	20.40
7	139.81[a]	136.06	15	19.50	19.10
8	160.36	160.43	16	12.73	12.77
8a	113.40	111.11	17		53.45
9	185.97	181.14			

[a] Assignments may be reversed.

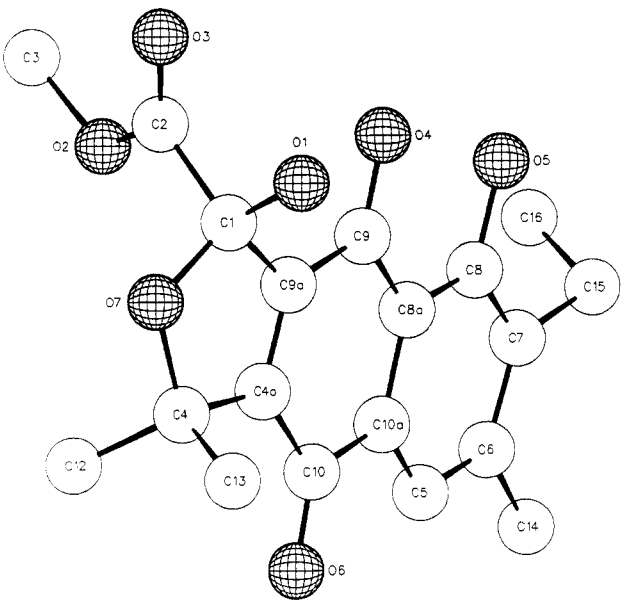


Figure 1. Computer-generated perspective drawing of annulin A (**3**). Hydrogen atoms are omitted for clarity.

ppm in the ^{13}C NMR spectrum of annulin A (Table II).

The remaining functionality in annulin A could be readily identified from its spectral data. ^{13}C NMR resonances at 169.35 and 54.04 ppm, in conjuction with the ^{1}H NMR resonance at 3.87 ppm and an IR band at 1750 cm^{-1}, indicated a methyl ester. A ^{13}C NMR resonance at 101.45 ppm and a ^{1}H NMR resonance at 4.92 ppm (brs, 1 H) were assigned to a hemiketal, while a ^{13}C NMR resonance at 89.08 ppm was assigned to a tertiary ether carbon.

The complete structure of annulin A (**3**) was solved by single-crystal X-ray diffraction analysis. A computer-generated drawing of the final X-ray model of annulin A (**3**) is given in Figure 1. Annulin A is a naturally occurring racemate, and the enantiomer shown is arbitary. The only chiral center, C1, is a hemiketal that presumably epimerizes in solution. The five-membered ring is essentially planar; all internal torsional angles are less than 10°. Thus, the tricyclic portion of annulin A is planar within experimental error. There appear to be intramolecular hydrogen bonds between O3–HO1 and O4–HO5. As expected, the ethyl side chain is rotated out of the molecular plane by roughly 90°.

Annulin B (**4**) was obtained as an optically active orange oil that gave a parent ion in the HREIMS that agreed with a molecular formula of $C_{21}H_{22}O_7$ (M^+ 386.1361, calcd 386.1366). The ^{1}H NMR spectrum of annulin B again revealed the presence of a napthoquinone substructure containing hydroxyl, ethyl, and methyl substituents on the

aromatic ring as in annulin A (3) (Table I). Support for this fragment came from IR bands at 1657 and 1638 cm^{-1} assigned to the quinone carbonyl stretching vibrations, a base-induced bathochromic shift to 530 nm in the UV/visible spectrum, and ^{13}C NMR resonances at 181.14 and 178.62 ppm assigned to the quinone carbonyl carbons.

Functionality accounting for the remaining atoms in annulin B ($C_8H_{12}O_4$) was identified from its spectral data. ^{13}C NMR resonances at 167.68 and 53.45 ppm, a ^1H NMR resonance at 3.76 ppm (s, 3 H), and an IR band at 1757 cm^{-1} identified a methyl ester. ^1H NMR resonances at 1.49 (s, 3 H), 1.51 (s, 3 H), and 1.85 (s, 3 H) ppm could be assigned to three aliphatic methyl groups, and a gated decoupled ^{13}C NMR spectrum of 4 contained resonances at 23.78 and 25.90 ppm that both appeared as quartets of quartets typical of a *gem*-dimethyl moiety. An IR band at 1738 cm^{-1} and a ^{13}C NMR resonance at 203.02 ppm were assigned to a ketone, and ^{13}C NMR resonances at 43.64 and 84.48 ppm were assigned to quaternary and oxygen-bearing tertiary carbons respectively.

The presumption of a common biogenesis for annulin B (4) and the rest of the *Garveia* metabolites led us to situate the ketone and the *gem*-dimethyl array at positions corresponding to C3 and C4 in the anthracene skeleton of the other metabolites. The chemical shift of the quaternary carbon resonance in the spectrum of 4 (43.6 ppm), which was close to that assigned to C4 (46.9 ppm) in 2, supported this placement. The chemical shift of the tertiary carbon (84.4 ppm) in the spectrum of annulin B was quite similar to the chemical shift of the C2 carbon in 2-hydroxygarvin A (2; 81.6 ppm), implying that it too was attached to an oxygen, a single alkyl, and two carbonyl carbons. Thus, the tertiary carbon in annulin B had to be attached to the ketone carbonyl at C3, the ester carbonyl, the remaining aliphatic methyl, and the remaining oxygen atom. The final site of unsaturation required by the molecular formula of annulin B could be generated by forming an ether linkage between the oxygen atom on C2 and an unsatisfied valence at C9a, resulting in the proposed structure 4 for annulin B.

A complete ^{13}C NMR assignment for annulin B (4) is given in Table II. The assignments were made from empirical calculations using juglone as a model. Of particular note are the resonances at 163.8 and 119.1 ppm assigned to C9a and C4a, respectively, which reflect the influence of the ether oxygen on the olefinic carbons of the quinone.

Annulins A (3) and B (4) both appear to be degradation products of garveatins. The conversion of garveatin B (6) to annulin B (4) requires oxidation of the central ring to a quinone, hydroxylation at C2, cleavage of the C1–C9a bond, and oxidation of the C1 carbon to a carboxylic acid. 2-Hydroxygarveatin B (7), a cooccurring metabolite,[3] is a possible intermediate in this pathway. Conversion of any potential garveatin precursor to annulin A (3) requires the removal of at least one carbon atom (C3) in addition to oxidation-state transformations.

Annulin A (3) and annulin B (4) both show antibacterial activities comparable to the other *Garveia* metabolites.

Experimental Section

^1H NMR spectra were recorded on Bruker WP-80, Varian XL-300, and Bruker WH-400 spectrometers. ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer. Me_4Si was used as an internal standard. Low-resolution mass spectra were recorded on an AEI MS902 spectrometer and high-resolution mass spectra on an AEI MS50 spectrometer. IR spectra were recorded on a BOMEM Fourier transform spectrometer. UV–visible spectra were recorded on a Bausch & Lomb Spectronic-2000 instrument. Optical rotation measurements were recorded on a Perkin-Elmer 141 polarimeter.

Merck silica gel (230–400 mesh) was used for flash and preparative thin-layer chromatography, and a Whatman Magnum-9 Partisil-10 column was used for preparative HPLC. Sephadex LH-20 was used for molecular exclusion chromatography. R_f's are listed for all compounds in an analytical TLC system using a 1:50:50 acetic acid/ethyl acetate/hexane eluent.

Collection Data. *G. annulata* was collected by hand using SCUBA (−2 to −9 m) on exposed rocky reefs in Barkley Sound, Vancouver Island, British Columbia, during the winter and spring months.

Extraction and Chromatography. Freshly collected whole specimens were immediately placed in methanol and stored at room temperature. The methanol extract was decanted and filtered through Celite. The filtrate was evaporated in vacuo to give an aqueous suspension that was diluted to 400 mL with distilled water and extracted successively with hexane (3 × 400 mL), methylene chloride (3 × 400 mL), and ethyl acetate (2 × 400 mL).

The hexane (600 mg) and methylene chloride (4 g) extracts were fractionated separately by step-gradient vacuum flash chromatography using a 3.5-cm-thick silica pad in a sintered-glass funnel (10-cm diameter). Fractions eluting with the same solvent composition from each separation were combined. Elution with 20% ethyl acetate/hexane, 50% ethyl acetate/hexane, 100% ethyl acetate, and 20% methanol/ethyl acetate gave fractions A (140 mg), B (500 mg), C (1.5 g), and D (700 mg), respectively.

Flash fraction B was evaporated to dryness and chromatographed on LH20 (90% methanol/methylene chloride; 1 m × 4 cm column). The major peak contained a mixture of compounds with R_f's close to 0.5. Preparative silica gel TLC of the mixture (50% ethyl acetate/hexane) yielded two fractions, P1 and P2. Further TLC purification of P1 (2% methanol/chloroform) yielded impure annulin A and pure annulin B (4; 12 mg). Normal-phase HPLC (40% ethyl acetate/hexane) gave pure annulin A (3; 20 mg). When spotted on a TLC plate and subjected to the vapours of a 25% aqueous ammonia solution, annulin A (3) turned a dark purple while annulin B (4) went bright pink.

Annulin A (3): Orange crystals from 95% ethanol; R_f 0.51; UV, λ_{max} (MeOH) 217 nm, 247 439, (MeOH + NaOH) 286, 559; ^1H NMR (300 MHz, $CDCl_3$) 1.14 (t, 3 H, J = 7 Hz), 1.63 (s, 3 H), 1.72 (s, 3 h), 2.44 (s, 3 H), 2.76 (q, 2 H, J = 7 Hz), 3.87 (s, 3 H), 4.92 (br s, 1 H), 7.47 (s, 1 H), 12.12 (s, 1 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 185.97, 180.92, 169.35, 160.32, 154.29, 145.63, 140.76, 139.81, 130.37, 122.23, 122.10, 113.40, 101.45, 89.08, 54.04, 27.94, 26.43, 20.09, 19.50, 12.73 ppm; IR ($CHCl_3$) 1749.9, 1657.2, 1616.1 cm^{-1}; MS, m/z (rel intens) 360 (M^+, 6), 342 (2), 327 (1), 301 (45), 283 (100), 255 (14); exact mass for $C_{19}H_{20}O_7$, calcd 360.1209, found 360.1221.

Annulin B (4): Orange oil; R_f 0.51; $[\alpha]_D$ +8.0° (c 0.2, $CHCl_3$); UV, λ_{max} (MeOH) 208 nm, 255, 293, 425, (MeOH + NaOH) 235, 270 (sh), 307 (sh), 530; ^1H NMR (300 MHz, $CDCl_3$) 1.15 (t, 3 H, J = 7 Hz), 1.49 (s, 3 H), 1.51 (s, 3 H), 1.85 (s, 3 H), 2.42 (s, 3 H), 2.73 (q, 2 H, J = 7 Hz), 3.76 (s, 3 H), 7.1 (s, 1 H), 12.35 (s, 1 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 203.02 (s), 181.14 (s), 178.62 (s), 167.68 (s), 163.79 (s), 160.43 (s), 147.64 (s), 136.06 (s), 127.59 (s), 120.65 (d), 119.11 (s), 111.11 (s), 84.48 (s), 53.45 (q), 43.64 (s), 25.90 (q), 23.78 (q), 20.40 (q), 20.38 (q), 19.10 (t), 12.77 (q) ppm; IR ($CHCl_3$) 1757, 1736, 1657, 1638 cm^{-1}; MS, m/z (rel intens) 386 (M^+, 17), 358 (25), 343 (100), 283 (17); exact mass for $C_{21}H_{22}O_7$, calcd 386.1366, found 386.1361.

Garvatin B Quinone (5): Red oil; R_f 0.63; UV, λ_{max} (MeOH) 208 nm 231, 283, 416; ^1H NMR (400 MHz, $CDCl_3$) 1.16 (t, J = 7 Hz, 3 H), 1.61 (s, 3 H), 1.97 (s, 3 H), 2.45 (s, 3 H), 2.78 (q, J = 7 Hz, 2 H), 7.51 (s, 1 H), 11.79 (s, 1 H), 11.84 (s, 1 H) ppm; MS, m/z (rel intens) 340 (M, 100), 326 (20), 312 (44), 297 (38), 284 (51), 269 (55), 266 (42); exact mass for $C_{20}H_{20}O_5$, calcd 340.1311, found 340.1306.

Single-Crystal X-ray Analysis of Annulin A (3). Excellent crystals of annulin A could be grown from 95% ethanol. Preliminary X-ray photographs showed only triclinic symmetry and accurate lattice constants of a = 5.635 (2), b = 10.530 (2), c = 15.448 (5) Å; and α = 74.78 (2), β = 82.51 (3), γ = 89.59 (2)°. If

(3) Fahy, E.; Andersen, R. J., submitted for publication in *Can. J. Chem.*

this unit cell contained 2 molecules of composition $C_{19}H_{20}O_7$, a perfectly reasonable crystal density of 1.37 g/cm^3 would result. The space group could be either $P1$ or $P\bar{1}$, and the latter centrosymmetric choice was the correct one. All unique diffraction maxima with $2\theta < 114°$ were collected using graphite monochromated Cu K$\bar{\alpha}$ radiation and variable-speed, 1° in ω scans. Of the 2359 unique reflections surveyed in this manner, 1440 (61%) were judged observed [$F_o > 3\sigma(F_o)$].[4] A phasing model was found with the MULTAN series of programs, and the initial E synthesis revealed all of the non-hydrogen atoms. Hydrogens were located on a ΔF synthesis following partial refinement. Block-diagonal least-squares refinements with anisotropic nonhydrogen atoms and isotropic hydrogens have converged to a conventional crystallographic residual of 0.0416 for the observed reflections. Additional crystallographic details can be found in the supplementary material.

Antimicrobial Activity. A standard in vitro disk (0.25 in.) bioassay was used to assess the antibacterial activity of the annulins. Activities are reported as minimum inhibitory concentrations (MIC) in μg/disk. *Staphylococcus aureus*: A (**3**), 31.5; B (**4**), 7.5. *Bacillus subtilis*: A (**3**), 6.3; B (**4**), 1.5.

Acknowledgment. We thank Mike LeBlanc and the staff of the Bamfield Marine Station for assistence with collecting *G. annulata*. Financial support at UBC was provided by grants to R.J.A. from the Natural Sciences and Engineering Research Council of Canada, the National Cancer Institute of Canada, and Rohm and Haas. The Cornell authors thank the New York State Sea Grant, NSF INT14133 and NIH CA24487, for financial support.

Registry No. **3**, 105335-73-7; **4**, 105335-74-8; **5**, 105335-75-9.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, interatomic distances, interatomic angles, and torsional angles for annulin A (**3**) (5 pages). Ordering information is given on any current masthead page.

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Photochemistry of 5- and 6-Iodouracils in the Presence of Allylsilanes and Alkenes. A Convenient Route to C5- and C6-Substituted Uracils[1]

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The photocoupling reaction of 5- and 6-iodouracil derivatives with allylsilanes and alkenes is presented. Irradiation of 5-iodouridine (**5**) and 5-iodo-2′-deoxyuridine (**6**) in the presence of allyltrimethylsilane in aqueous acetonitrile gave 5-allyluridine (**7**) and 5-allyl-2′-deoxyuridine (**8**), respectively. Irradiation of 6-iodo-1,3-dimethyluracil (**11**) in the presence of allylsilanes and alkyl-substituted olefins produced the corresponding C6-substituted uracil derivatives in good yields. 5-Fluoro-6-iodo-1,3-dimethyluracil (**12**) underwent a similar photocoupling reaction with allylsilanes and alkenes. The photocoupling reaction provides a convenient method for carbon–carbon bond formation at the C5 or C6 position of uracil derivatives. A radical addition mechanism has been proposed for this novel photocoupling reaction.

Synthetic methods for carbon–carbon bond formation at the C5 or C6 position of pyrimidine bases and nucleosides have become increasingly important in recent years because of a broad spectrum of biological activities of these derivatives.[2,3] The palladium-catalyzed coupling of alkenes[4] and alkynes[5] with 5-chloromercuri- or 5-iodouridine derivatives initially described by Bergstrom and co-workers has been widely used for the synthesis of C5-substituted uracil nucleosides with carbon functionalities.[3] Organolithium derivatives of pyrimidine bases and nucleosides have also been used for carbon–carbon bond formation at the C6 position of protected uridine derivatives.[3,6] A different approach utilizing a photochemical reaction as the key step has also been reported.[7,8] For example, photocycloadducts of 5-fluorouracil derivatives with alkenes were utilized for the preparation of C5-substituted uracil derivatives.[8]

In the course of our studies on the organic photochemistry of nucleic acid bases,[9] we recently demonstrated that photoaddition of alkenes and alkynes to 6-cyanouridine provides a useful route to C5-substituted uridines possessing functionalized side chains.[10] We have sought a

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