(1.471 for reversal enantiomorph) with N = number of Bijvoet pairs, $R_o = \Delta I_o / \langle F_o^2 \rangle$, $R_c = \Delta I_c / \langle F_c^2 \rangle$, $\Delta I_o = F_o^2(+h) - F_o^2(-h)$, and $\Delta I_c = F_c^2(+h) - F_c^2(-h)$.

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Registry No. 1, 71774-90-8; 2, 70544-92-2; 3, 71774-91-9; 4, 70544-90-0; 5, 64756-04-3.

Supplementary Material Available: A list of bond distances, bond angles, deviations of atoms from the ring planes, and torsion angles (3 pages). Ordering information is given on any current masthead page.

Syntheses of 7,12-Dimethylbenz[*a*]anthracene-3,4- and -1,4-diones[1]

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In view of the recent communication[3] in which the synthesis of 7,12-dimethylbenz[*a*]anthracene-3,4-dione (1) by oxidation of 3-hydroxy-7,12-dimethylbenz[*a*]anthracene (2) with benzeneselenic anhydride was described, we thought it of interest to report some of our results in the same area.

We have oxidized **2**[4] with Fremy's salt[5] to obtain pure **1**, mp 154–155 °C, in 72% yield calculated on the recovery of 22% of **2**. We made no attempt to reduce **1** to 3,4-dihydro-3,4-dihydroxy-7,12-dimethylbenz[*a*]anthracene[3] but did reduce **1** to 3,4-dihydroxy-7,12-dimethylbenz[*a*]anthracene (**3**) in almost quantitative yield by sodium dithionite.

In a similar way 1-hydroxy-7,12-dimethylbenz[*a*]anthracene[4] (**4**) was oxidized to 7,12-dimethylbenz[*a*]anthracene-1,4-dione (**5**) in 94% yield based on recovery of 47% of **4**, and **5** was reduced to 1,4-dihydroxy-7,12-dimethylbenz[*a*]anthracene (**6**). The yields of **1** and **5** were not increased by using larger amounts of Fremy's salt, and unchanged **2** and **4** were always recoverable in about the amounts mentioned above. Interestingly, 2-hydroxy- and 4-hydroxy-7,12-dimethylbenz[*a*]anthracenes[4] were recovered unchanged on treatment with Fremy's salt, probably because oxidation would require attack at the hindered 1-position. A similar failure of enzymic hydroxylation of 7,12-dimethylbenz[*a*]anthracene to yield appreciable amounts of 1,2-dihydro 1,2-diols has been noted, 5,6-dihydro diols, 3,4-dihydro diols, 8,9-dihydro diols, and 10,11-dihydro diols being the products.[6]

The 3-hydroxy-7,12-dimethylbenz[*a*]anthracene (**2**) we used was prepared by a new route, shown in Scheme I, which we regard as preferable to the other syntheses of **2**.[3,4]

The starting materials for our present synthesis of **2** were two readily available chemicals, namely, phthalic anhydride and 2-bromo-6-methoxynaphthalene.[7] Condensation via the Grignard reagent afforded *o*-(6-methoxy-2-naphthoyl)benzoic acid[8] (**7**) in 65% yield. The remaining steps to 3-hydroxy-7,12-dimethylbenz[*a*]anthracene (**2**) went well as indicated in Scheme I.

Experimental Section[9]

***o*-(6-Methoxy-2-naphthoyl)benzoic Acid (7).** In the best of several experiments a hot solution of 11.85 g of 2-bromo-6-methoxynaphthalene in 150 mL of benzene was added to a suspension of 1.21 g of sublimed magnesium in 50 mL of 1:1 ether–benzene containing 0.5 mL of ethylene dibromide[10] during 30 min. After reflux was maintained for 15 h the Grignard reagent was added to a stirred suspension of 8.88 g of phthalic anhydride in 100 mL of 1:1 ether–benzene. After 4 h at reflux the mixture was cooled, treated with dilute HCl, and worked up as usual to yield 11.3 g (72%) of **7**, mp 164–166 °C. Recrystallization from benzene yielded **7**, mp 169–170 °C, with little loss.[8] In a similar run starting with 47.4 g of bromo compound a somewhat lower yield was obtained.

3-Methyl-3-(6-methoxy-2-naphthyl)phthalide (8).[12] To a solution of 6.0 g of **7** in 100 mL of 1:1 ether–THF was added 32 mL of 1.6 M methyllithium (Ventron). After refluxing for 15 h the mixture was worked up as usual to yield 5.5 g (91%) of **8**, mp 159–161 °C.

***o*-[1-(6-Methoxy-2-naphthyl)ethyl]benzoic Acid (9).**[12] A mixture of 4.56 g of **8**, 30 g of zinc dust activated with 0.5 g of $CuSO_4$, 25 mL of pyridine, and 240 mL of 10% KOH was held at reflux for 15 h and worked up to yield 4.4 g (97%) of **9**, mp 207–208 °C.

3-Methoxy-7,12-dimethylbenz[*a*]anthracene (11). Ten milliliters of anhydrous HF was stirred in 0.55 g of **9**. After 15 min the solution was poured on ice and worked up as usual to yield a yellow viscous oil which was dissolved in 10 mL of ether and treated with 3 mL of 1.5 M methyllithium. After 15 h of refluxing, the crude product was chromatographed over neutral alumina using benzene to yield 450 mg (87%) of **11**,[4] mp 131–132 °C.

***o*-[1-(6-Methoxy-2-naphthyl)ethyl]acetophenones (10).**[12] To a solution of 1.4 g of **9** in 30 mL of THF was added 10 mL of 1.5 M CH_3Li. After 5 h at reflux the mixture was treated with dilute HCl and after removal of the THF on a rotary evaporator there was obtained an almost quantitative yield of **10**, mp 106–107.5 °C.

Attempts to cyclize **10** to **11** with PPA (room temperature for 7 h gave 65% of **11**), with HF for 15 min (37% of **11**), or with $CF_3CO_2H + ZnCl_2$ at reflux for 4 h (42% of **11**) did not afford **11** in as high a yield as was obtained by the benz[*a*]anthrone route above described.

7,12-Dimethylbenz[*a*]anthracene-3,4-dione (1).[12] A solution of 3.0 g of Fremy's salt and 1.36 g of **2**[4] in 50 mL of $^1/_6$ M KH_2PO_4, 400 mL of water, and 400 mL of methanol was stirred for 15 h

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[2] Postdoctoral Research Associate

[3] Sukumaran, K. B.; Harvey, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 1353.

[4] Newman, M. S.; Khanna, J. M.; Kanakarajan, K.; Kumar, S. *J. Org. Chem.* **1978**, *43*, 2553. The melting point of **11** is given as 131–132 °C.

[5] Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley-Interscience: New York, 1967; Vol. 1, p 940.

[6] Tierney, B.; Hewer, A.; MacNicoll, A. D.; Gervasi, P. G.; Rattle, W.; Walsh, C.; Grover, P. L.; Sims, P. *Chem.-Biol. Interact.* **1978**, *23*, 243.

[7] French, H. E.; Sears, K. *J. Am. Chem. Soc.* **1948**, *70*, 1279.

[8] Weizmann, C.; Bergmann, E.; Bergmann, F. *J. Chem. Soc.* **1935**, 1367 give a melting point of 166 °C for **7**.

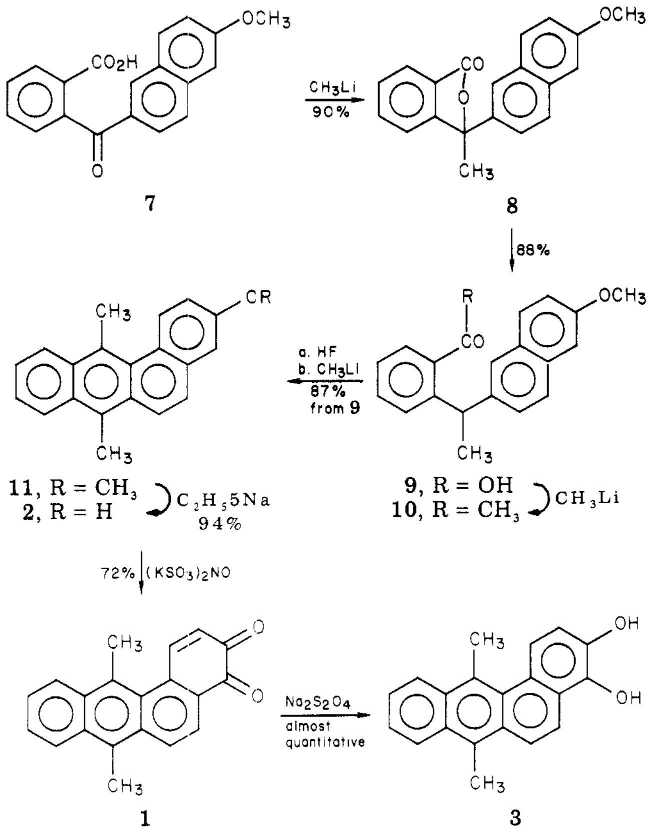
[9] All melting points are uncorrected. The term "worked up as usual" means that an ether–benzene solution of the reaction products was washed with acid and/or base to separate acidic and neutral products. The solvents were then removed on a rotary evaporator or by distillation. In general the IR, NMR, and mass spectra were taken and agreed with those expected from the structures.

[10] Pearson, D. E.; Cowan, D.; Beckler, L. D. *J. Org. Chem.* **1959**, *24*, 504.

[11] This quinone, **1**, was reported[3] to melt at 181–183 °C. However, Dr. Harvey has informed us that a deteriorated sample was involved and that the true melting point of **1** is 155–156 °C as we found.

[12] These new compounds gave analyses within ±0.3% of the theoretical C and H.

Scheme I



at room temperature. The dark green solid produced was collected and chromatographed over silica gel using benzene to produce 300 mg (22%) of **2** from the early fractions and 800 mg (72% based on the recovery of **2**) of **1**, mp 155.5–156.5 °C.[11]

3,4-Dihydroxy-7,12-dimethylbenz[*a*]anthracene (3).[12] To a well-stirred solution of 200 mg of **1** in 100 mL of benzene saturated with N_2 was added under N_2 a solution of $Na_2S_2O_4$ in 30 mL of water. After 15 min (the blue color changed to yellow in a few minutes) the usual workup afforded 180 mg (90%) of **3**, mp 174–175 °C, as pale yellow crystals.

7,12-Dimethylbenz[*a*]anthracene-1,4-dione (5).[12] By a procedure entirely analogous to the oxidation of **2** to **1**, 3.0 g of **4**[4] was oxidized by 9.0 g of Fremy's salt to give 1.47 g (94% based on recovery of 47% of **4**) of **5**, mp 199–201 °C, as deep violet crystals.

1,4-Dihydroxy-7,12-dimethylbenz[*a*]anthracene (6).[12] By a method entirely analogous to that used in the reduction of **1** above there was obtained 180 mg (90%) of **6**, mp 114–116 °C.

Registry No. **1**, 70092-13-6; **2**, 57266-83-8; **3**, 71964-72-2; **4**, 66240-13-9; **5**, 71964-73-3; **6**, 71964-74-4; **7**, 71964-75-5; **8**, 71964-76-6; **9**, 71964-77-7; **10**, 71974-97-5; **11**, 66240-02-6; 2-bromo-6-methoxynaphthalene, 5111-65-9; phthalic anhydride, 85-44-9.

Two Novel Lactams from the Marine Sponge *Halichondria melanodocia*

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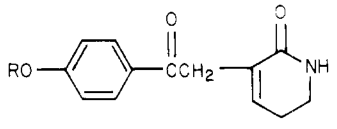
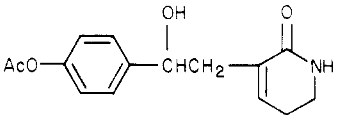
Although one of the earliest marine natural products to be extracted and used commercially, Tyrian purple, proved to be an indole derivative,[1] few other indole-related compounds have been reported among the numerous marine metabolites described in the past two decades.[2] Quite recently, however, several indoles and indole-based compounds have been isolated from sponges[3] and algae.[4] In this note we report the isolation of two novel lactams, one of them an indole derivative, from an algae-infested Carribean sponge, *Halichondria melanodocia*.[5]

Specimens of *H. melanodocia* were collected at 2–4 ft depths near Summerland Key, Fla. The new lactams were obtained from isopropyl alcohol extracts of the wet sponge through a sequence of solvent partitioning followed by chromatography over Sephadex LH-20 and finally silica gel. Crystallization of one of the fractions from the silica gel chromatography yielded a white solid, **1a**, mp 235.0–235.5 °C, $C_{13}H_{13}NO_3$ (high resolution mass spectrum 231.087; calcd 231.089). The infrared spectrum (KBr) of **1a** showed absorption at 3377 (sharp, OH), 3200 (brd, NH), 1680 (sh at 1689), and 1635 cm^{-1}, consistent with hydroxyl, α,β-unsaturated ketone, and primary amide groups. The ultraviolet absorption spectrum showed maxima at 273 (ϵ 20 600) and 218 nm (ϵ 17 800), indicative of a *p*-hydroxybenzoyl moeity.[6] Further evidence for this structural feature was obtained from the ^1H NMR spectrum ($CDCl_3$–CD_3OD) which contained a pair of two-proton doublets at δ 6.86 and 7.92 (J = 9 Hz) and also the mass spectrum which exhibited a base peak at 121 (high resolution mass spectrum 121.028; calcd for $C_7H_5O_2$ 121.029).



1a, R = H
b, R = Ac



2

In addition to the aromatic proton signals, the downfield region of the ^1H NMR spectrum of **1a** contained a one-proton triplet signal at 6.56 ppm (J = 4 Hz) attributable to the β proton of an α,β-unsaturated carbonyl system. This proton was coupled to a broad two-proton multiplet at δ 2.44 (overlapping dt J = ~4, ~7.5 Hz), which in turn was coupled to a two-proton triplet appearing at δ 3.46 ppm ($J \simeq$ 7.5 Hz). Irradiation of the signal at 2.44 not only collapsed the triplets at δ 6.56 and 3.46 to singlets, but also sharpened a broad two-proton singlet at δ 3.92. Hence, the methylene groups resonating δ 2.44 and 3.92 were confirmed to have a homoallylic relationship. These chemical shifts and proton interrelationships were best accounted for by the partial structure $-CH_2C(CO)=$

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(4) (a) M. R. Brennan and K. L. Erickson, *Tetrahedron Lett.*, 1637 (1978); (b) G. T. Carter, K. L. Rinehart, Jr., L. H. Li, S. L. Kuentzel, and J. L. Connor, *ibid.*, 4479 (1978).

(5) F. Wiedenmayer, "Shallow-Water Sponges of the Bahamas", Birkhauser Verlag, Basel, 1977, p 149.

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