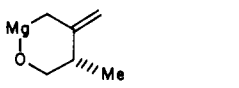
characterizations of the individual components of these mixtures (when possible), combined with compelling literature precedents, we conclude that the stereo- and regioselectivities implicit in Scheme I are very high. In any event, we obtained analytically pure (+)-3 in 16–20% overall yield from (*S*)-(−)-perilla aldehyde (**5**).[12-14]

Key intermediate **4** was prepared enantiomerically pure from known alcohol **13**[15] as follows. Oxidation of **13** (Jones reagent/acetone) followed by methyl ketone formation [(1) 1.5 equiv of $(COCl)_2$/benzene, (2) 3 equiv of Me_2CuLi/Et_2O, −78 °C] afforded **14** in 75–80% yield. Wittig olefination ($Ph_3P{=}CH_2$/THF) and reductive debenzylation (Li/NH_3) provided **4** (55–60% yield from **14**).

With **3** and **4** in hand we were ready to effect the critical connection. Treatment of alkenol **4** with 2.0 equiv of Schlosser's base (*t*-BuOK/*n*-BuLi/hexane, 0 °C)[16] followed by $MgBr_2$/THF afforded a milky solution of a dianion that we are tempted to formulate as **15**. Addition of "**15**" (3.5 equiv) to **3** (Et_2O/−60 °C) provided **16**. Crude **16** was induced to spiroketalize (3.0 equiv of $ZnCl_2/CH_2Cl_2$, −20 °C), producing **17** and **18** (48:1) in 69% combined yield from lactone **3**.[17]



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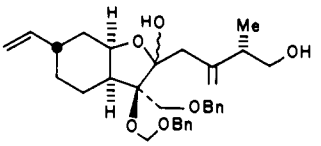

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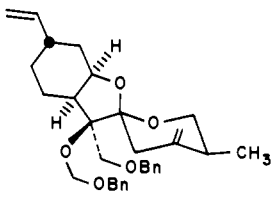

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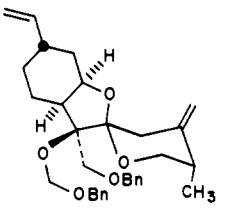

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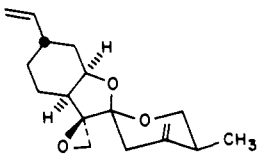
Completion of the synthesis proceeded uneventfully as follows. The epoxide moiety could be prepared in 82% yield by sequential treatment of **17** with (1) Li/NH_3, (2) $MsCl/NEt_3$, and (3) DBU/benzene.[18] The two latent carbonyl moieties in resulting diene **19** were ummasked oxidatively by using the method of Sharpless ($RuCl_3{\cdot}3H_2O/NaIO_4/H_2O/CH_3CN/CCl_4$).[19] Acid **20** was esterified (CH_2N_2), and the resulting keto ester **21** was reduced with high axial selectivity (KS-Selectride/THF, 0 °C; axial/equatorial = 450:1)[20] to provide alcohol **22** in 42% yield overall from **19**. Cinnamoylation (*trans*-PhCH=CHCOCl/CH_2Cl_2/C_5H_5N/DMAP) afforded material that was indistinguishable from natural (+)-phyllanthocin (**2**) by routine spectroscopic and analytical techniques.[12-14]



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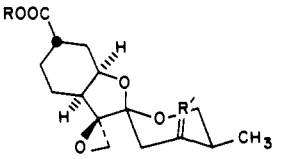

20 R=H; R'=O
21 R=CH_3; R'=O
22 R=CH_3; R'=H, axial OH

Acknowledgment. We thank Cornell University, the Research Corp., and the National Institutes of Health (GM/CA 30350-01) for their generous support of this work. P.R.M. thanks the National Institutes of Health for a predoctoral fellowship, and D.B.C. thanks the E. I. du Pont de Nemours Co. for a young faculty fellowship. Our gratitude is expressed to Professor G. R. Pettit and Dr. Noal Cohen for providing samples of phyllanthocin and (*S*)-(+)-3-hydroxy-2-methylpropanoic acid, respectively. Acknowledgment is made to the National Science Foundation Instrumentation Program (CHE 7904825 and PCM 8018643) for support of the Cornell Nuclear Magnetic Resonance Facility.

Registry No. 2, 62948-37-2; **3**, 82167-72-4; **4**, 82189-55-7; **5**, 18031-40-8; **6**, 82167-73-5; **7**, 82167-74-6; **8**, 82167-75-7; **9**, 82167-76-8; (3*R*)-**10**, 82167-77-9; (3*S*)-**10**, 82167-78-0; **11**, 82182-03-4; **13**, 63930-46-1; **14**, 82167-79-1; **16**, 82167-80-4; **17**, 82167-81-5; **18**, 82189-56-8; **19**, 82167-82-6; **20**, 82167-83-7; **21**, 82167-84-8; **22**, 82167-85-9; *trans*-PhCH=CHCOCl, 17082-09-6; (*S*)-(+)-3-hydroxy-2-methylpropanoic acid, 26543-05-5.

Supplementary Material Available: IR, ^{13}C NMR, and 300-MHz ^1H NMR data for key intermediates (3 pages). Ordering information is given on any current masthead page.

(12) All compounds were purified by flash chromatography [Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923]. Compounds depicted as mixtures were characterized by IR, 90-MHz ^1H NMR, and low-resolution mass spectroscopy. The two epimeric lactones depicted by formula **10** and all subsequent intermediates were characterized by IR, 300-MHz ^1H NMR, and carbon-13 NMR spectroscopy, high-resolution MS or C, H analysis, optical rotation, and melting point (ref 13).

(13) Detailed experimental procedures and spectroscopic data will be reported in a forthcoming publication. Selected spectroscopic data are provided as supplementary material.

(14) The optical purities of **3**, **4**, and synthetic and natural **2** were checked by a standard literature procedure [see: Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543].

(15) Alcohol **13** has been prepared from (*S*)-(+)-3-hydroxy-2-methylpropanoic acid by standard procedures: Collum, D. B.; McDonald, J. H., III; Still, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2118 (see ref 13).

(16) Schlosser, M.; Hartmann, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508.

(17) This is a thermodynamically controlled ketalization; identical product distributions can be obtained by equilibration of **17** or **18** under the reaction conditions.

(18) Grieco, P. A.; Oguri, T.; Burke, S. *J. Org. Chem.* **1978**, *43*, 4552.

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(20) Determined by digitally integrated gas chromatographic comparison with an authentic sample of the equatorial isomer.

Delesserine, a New Metabolite of Mixed Biogenesis from the Red Marine Alga *Delesseria sanguinea* (Lamouroux)

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In the past decade, the number of newly discovered metabolites from marine organisms has rapidly increased; however, very few are derived from the secondary sugar metabolism. We now report on the isolation and structure elucidation of such a new metabolite, delesserine (**1**), without any equivalent from other marine sources

(1) Supported by a CNRS grant (bourse Ingenieur–Docteur) from ICSN.

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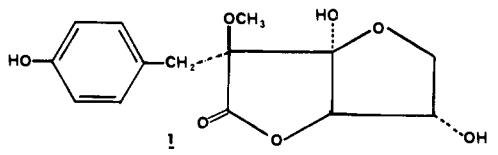


1

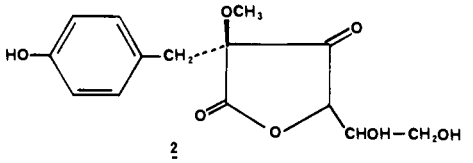
and with very few analogues among naturally occurring compounds. To our knowledge only piptoside,[2,3] ascorbigen,[4] and to a lesser extent conocarpine[5] and leucodrin[6] display some common features with delesserine (1). The compound was isolated from the marine alga *Delesseria sanguinea*,[7] belonging to the family Delesseriaceae. This family has, as yet attracted relatively little attention from marine natural products chemists,[8] despite the powerful anticoagulant properties displayed by the aqueous extracts of *D. sanguinea*.[9]

The ether-soluble material of the water–ethanol extract of *D. sanguinea*[10] gave some polar compounds. From this mixture the purification of delesserine (1) was achieved by a multiple-step procedure including chromatography on sephadex LH20 and silica gel and by HPLC on C_{18}-bondapak (H_2O–CH_3CN–MeOH, 75:20:5).

Delesserine (1) ($[\alpha]^{20}_D$ + 36° (*c* 0.72, MeOH)) was obtained as an amorphous powder which gave crystals from MeOH (mp 117 °C). The elemental composition $C_{14}H_{16}O_7$ was determined from high-resolution mass spectrometry (calcd for $C_{14}H_{16}O_7$ 296.0896, found 296.0895). The presence of a *para*-hydroxybenzyl moiety was deduced from the mass spectrum (*m/e* 107, C_7H_7O), from UV (λ_{max} (EtOH) 225 (15 000), 277 (4500); λ_{max} (EtOH/KOH) 220 (35 000), 293 (3000)), from ^1H NMR (δ 6.75 (d), 7.17 (d)), and from ^{13}C NMR (δ 157.9, 134.8 (2C), 128.1, 118.3 (2C)).[11] In addition, the presence of OH (IR 3400 cm^{-1}), lactone (IR 1770–1800 cm^{-1}, ^{13}C NMR δ 177.6), and OMe (^1H NMR δ 3.64 (s); ^{13}C NMR δ 55.8) were also established.

In fact, the ^{13}C NMR spectrum displayed signals for 28 carbons, suggesting that delesserine in solution exists in two forms. In view of this possibility, plus its lack of stability, an X-ray crystallographic study was performed on a single crystal obtained from MeOH. The structure of the crystalline form of delesserine was then determined to be **1** with the relative configuration shown.

In solution, as suggested above, delesserine exists in two forms by opening of the hemiketal function. The main form has structure **1**, while the minor form is the open form **2** as shown by the ^{13}C



2

NMR spectrum. Indeed, in this spectrum there were two different series of signals differing in relative intensity (which is, in fact, temperature dependent). Signals of the most intense series (δ 177.6, 157.9, 134.8, 128.1, 118.3, 111.4, 90.4, 87.2, 78.5, 75.9, 55.8, 38.3)[12] were assigned to the closed form **1**; signals of the minor series (δ 212.6, 177.0, 158.7, 134.8, 125.6, 118.8, 87.4, 85.3, 73.1, 64.2, 59.0, 44.5)[12] were due to the open form **2**. The structure of this form was secured by the presence of an ketone (δ 212.6) and a $CHOHCH_2OH$ group (δ 73.1, 64.2) similar to that of glycerol[13] and ascorbic acid.[14] The biosynthetic origin of delesserine is probably a condensation of a C^6–C^1 unit with a 3-dehydrohexonic acid moiety. A similar biosynthesis has been proposed for piptoside.[2] The biological properties of delesserine are currently under investigation.

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Registry No. 1, 82198-78-5; **2**, 82198-79-6.

Supplementary Material Available: X-ray crystal structure, positional and thermal parameters, final bond distances and angles, observed and calculated structure factors for **1**, and mass and ^1H NMR spectral data for delesserine (8 pages). Ordering information is given on any current masthead page.

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(7) Family Delesseriaceae; order Ceramiales; Subclass Florideae; class Rhodophyceae; phylum Rhodophyta.
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(10) The seaweeds was first collected in the Roscoff area (Brittany, France) in June 1978 and subsequently near "les tas de pois" (Brittany, France) in 1979 and 1980 springs. There was no significant variation in the chemical composition.
(11) For the main signals of the predominating form in solution.
(12) The ^{13}C NMR spectrum has been recorded in D_2O at 37 °C. The signals at 87.2 and 87.4 may be interchanged.
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Synthesis of a Cofacial Porphyrin–Quinone via Entropically Favored Macropolycyclization

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The precise, 3-dimensional orientation of molecular components achieved in macropolycyclic molecules makes them well-suited for use in model systems of biological processes.[1] The key role of porphyrin pigments and of quinones in the primary reactions of bacterial photosynthesis[2] provides impetus for the synthesis of porphyrin–quinone compounds. These syntheses have provided monosubstituted benzoquinone flexibly tethered or directly bonded to tetraphenylporphyrin.[3] However, the crucial requirements of distance and orientation in fast electron-transfer reactions[4] requires the synthesis of molecules with defined geometry, as occur in the photosynthetic systems.

We present the synthesis of a molecule containing a porphyrin and a quinone rigidly held 10 Å apart in cofacial parallel planes. Though capped,[5] bridged,[6] and cofacial[7] porphyrins have been

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