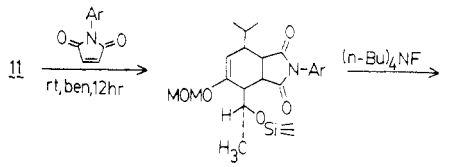
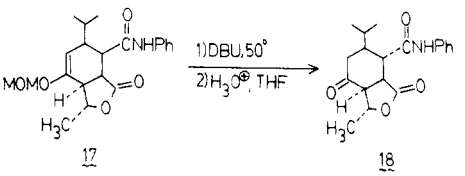
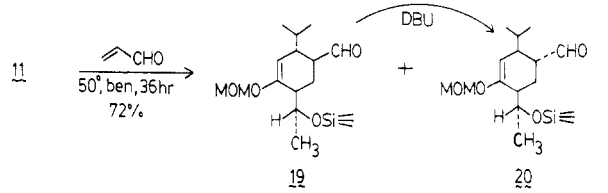
center which exhibits complete face selectivity in the intermolecular Diels–Alder reaction. While this product could be cleanly manipulated in a predictable fashion (**15** → **17** → **18**) none of these compounds revealed the relative stereochemistry between the preexisting exocyclic chiral center and the newly created ring chiral centers. For this





assignment we relied on an X-ray crystal structure of the bromo derivative **16**[21] derived from the Diels–Alder reaction of diene **11** with *N*-*p*-bromophenylmaleimide. This structure confirms that diene **11** and **13** exhibit the same facial selectivity in keeping with Franck's recently proposed selection rule.[2b] As just hypothesized the increased selectivity can be directly attributed to the presence of the *Z*-alkoxy substituent, which forces the reaction to proceed from conformer **11a** via the expected endo transition state. An additional, and perhaps undervalued, effect of the alkoxy substituent is to cant the transition state toward the carbon bearing the largest orbital coefficient.[22] In the case of alkoxy diene **11** this would maximize the effect of the chiral allylic carbon (see Chart I). It should be noted that the alkoxy substituent in diene **14** would distort the transition state away from the asymmetric centers which might be at least partially responsible for the decreased selectivity observed in that system.[2c,23]

Finally, in a more traditional vein, the alkoxy substituent can control the regiochemistry of the Diels–Alder reaction as evidenced by the addition of acrolein. The major product **19** was accompanied in this instance by a small amount of a minor isomer **20** (ratio 13:1). The identity



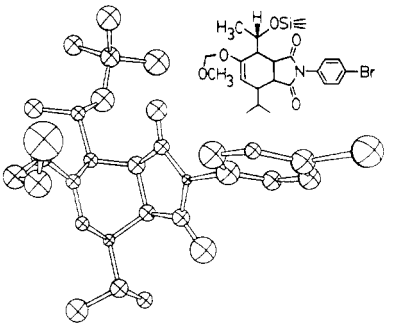
of this minor isomer was easily established by a base-catalyzed interconversion of **19** to **20**,[24] which confirmed that the face selectivity exhibited by diene **11** was again complete.

In conclusion the placement of an electron-donating substituent, such as an alkoxy group, cis to the chiral allylic carbon of a diene is unique in its ability to control both the stereoselectivity and regiochemistry of the intermolecular Diels–Alder reaction. Such systems are easily accessed by the direct β-lithiation of an alkoxy diene. The combination of these two methodologies accounts for the stereocontrolled introduction of five-contiguous asymmetric centers in two steps. Plans to utilize this strategy in natural product synthesis are currently under way in our laboratories.

Acknowledgment. This research was supported by a grant from Research Corporation. Acknowledgement is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(20) **15**: mp 117–119 °C (acetone/H_2O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.24–7.06 (3 H, m), 6.96 (1 H, dd, *J* = 7.0, 1.5 Hz), 4.75 (1 H, A of an AB, *J* = 6.3 Hz), 4.64 (1 H, dd, *J* = 4.5, 2.0 Hz), 4.62 (1 H, B of an AB, *J* = 6.3 Hz), 4.59 (1 H, dq, *J* = 10.2, 5.8 Hz), 3.54 (1 H, dd, *J* = 8.5, 4.5 Hz), 3.17 (1 H, dd, *J* = 8.5, 6.0 Hz), 3.07 (3 H, s), 2.23 (1 H, ddd, *J* = 10.2, 4.5, 2.0 Hz), 1.92 (1 H, dp, *J* = 10.2, 6.4 Hz), 1.66 (1 H, ddd, *J* = 10.2, 6.0, 4.5 Hz), 1.17 (3 H, d, *J* = 5.8 Hz), 1.01 (3 H, d, *J* = 6.4 Hz), 0.82 (3 H, d, *J* = 6.4 Hz).

(21) The ^1H NMR spectrum for **16** was identical with that for **15** except for the aromatic region. Crystals of **16** (mp 122–124 °C) suitable for X-ray analysis were obtained from acetone/water. The ORTEP drawing, minus hydrogens, is shown.



(22) For a discussion of the asymmetry of the transition state for the Diels–Alder reaction, see: Dewar, M. J. S.; Pierini, A. B. *J. Am. Chem. Soc.* **1984**, *106*, 203.

(23) The reversal of face selectivity for **14** relative to other asymmetric dienes is more difficult to rationalize.

(24) The epimerization of both **17** and **19** yields exclusively one isomer (**18** and **20**). This allows selective entry to either of two diasteromeric series.

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Bengamides, Heterocyclic Anthelminthics from a Jaspidae Marine Sponge

Summary: The methanol extract of an undescribed Fiji sponge contains the novel seven-membered ring heterocycles, bengamide A (**1a**) and bengamide B (**2a**), which are cyclized by a δ-hydroxylysine. These compounds are biotoxic to eucaryotic cells, nematodes, and bacteria.

Sir: During two past expeditions to the Fiji Islands we collected an abundant, finger-like, orange sponge, which is an undescribed member of the Jaspidae family (order Choristida = Astrophorida).[1] Chemical studies were in-

(1) An underwater photograph of this sponge is available from P.C., and a voucher specimen has been deposited in the UCSC IMS collection. Taxonomic examination of our voucher specimens revealed the following properties. The dermal membrane contains numerous asters; strongyles are irregularly distributed and tangential to the surface. The choanosome contains numerous asters. Strongyles occur in loose bunches; some of them are connected by spongin. The asters measure 15 to 30 μm in diameter. The strongyles, which are often curved are a variety of sizes, from 520 × 5 to 680 × 8 to 600 × 17 μm. The sponge is an undescribed genus in the Jaspidae. It may belong to the subfamily Jaspinae, but it has strongyles whereas all genera previously described in this subfamily have only oxeas as macroscleres.

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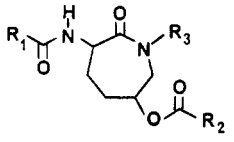
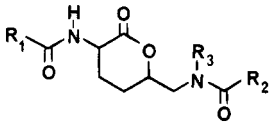
itiated on this sponge because the crude extract of a very small initial collection exhibited complete in vitro cytotoxicity to larynx epithelial carcinoma at 1.0 μg/mL, along with activity against the bacteria *Streptococcus pyrogenes* and the nematode *Nippostrongylus braziliensis*. A recollection of 1.4 kg of sponge from the Benga lagoon was immediately extracted with methanol, yielding 7.47 g of crude concentrate. Solvent partitioning of this crude oil (methanol vs. hexane, CCl_4, or CH_2Cl_2) concentrated the biological activity in the CCl_4 and CH_2Cl_2 fractions. Correspondingly, the ^{13}C NMR spectra of these same fractions revealed three prominent, complex compounds, bengamides A, B, and C, and a single amino acid (H-$\alpha \approx \delta$ 4.6) was one apparent subunit present in each bengamide.

Anthelminthic bioassay-guided isolation was utilized to follow purification of bengamides A and B from both the CCl_4 and CH_2Cl_2 fractions. At a concentration of 50 μg/mL, bengamides A and B were completely active against *Nippostrongylus braziliensis*. Antimicrobial activity, expressed as an MIC value in μg/mL, was also observed for both bengamides A and B: 3.9, 1.9 respectively, vs. *Streptococcus pyrogenes*.[2] Bengamide C has not yet been isolated in pure form; however, semipure fractions enriched in this compound displayed similar assay results, as described above.

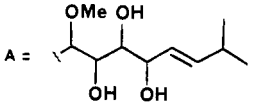
Similar structural features were presumed for bengamide A (1) and bengamide B (2) because of their nearly identical

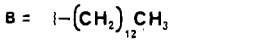


	R_1	R_2	R_3
1a (2a)	A	B	H (Me)
1b (2b)	B	A	H (Me)



	R_1	R_2	R_3
1c (2c)	A	B	H (Me)
1d (2d)	B	A	H (Me)





spectroscopic and chemical properties. The initial focus for structural elucidation was on bengamide A (mp 114–115 °C from MeOH; $[\alpha]^{20}_D$ +30.3° (*c* 0.081, MeOH); IR (neat) 3700–3100, 1740, 1660, 1650 cm^{-1}), and a single ring was obvious from its molecular formula of $C_{31}H_{56}O_8N_2$ (FAB mass spectrometry, $M^+ + H = 585$)[3,4] compared to

(2) Bioassay data were kindly provided by Dr. T. Matthews at Syntex Research.

Table I. Selected NMR COSY Results

compounds 1 and 2 ^1H–^1H ($CDCl_3$ and $CDCl_3/C_6D_6$, 50%) regular		compound 2 ^{13}C–^1H (CD_3OD) long range	
Me-1, -15	H-2	C-8	OMe
H-2	H-3	C-9	H-7, -10
H-3	H-4	C-16	H-10, -11, -11′, -14′, NMe
H-4	H-5	C-17	H-18, -18′
H-5	H-6		
H-6	H-7		
H-7	H-8		
Ha	H-10		
H-10	H-11, -11′		
H-11, -11′	H-12, -12′		
H-12, -12′	H-13		
H-13	H-14, -14′		
H-14, -14′	Hb[a]		
H-18, -18′	H-19, -19′		
H-19, -19′	H-20 to H-29		
H-20 to H-29	Me-30		

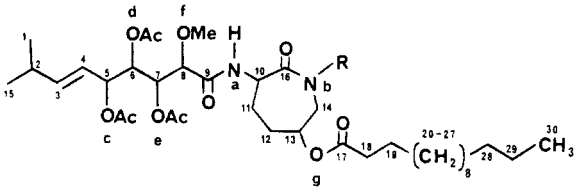
[a] Only in 1.

the count of unsaturated sites. The multiple bond moieties were identified from ^{13}C NMR[5] (Table A, supplementary material) and included one ester (174.2 s, 70.9 d), two amides (173.0 s, 172.3 s, 51.5 d, 45.2 t), and an (*E*)-CHCH=CHCH- array (141.9 d, 125.5 d, (^1H)^3J = 15 Hz). Additional functional groups were as follows: (a) three -CH(OH)- groups (74.3 d, 72.8 d, 72.5 d), (b) a -CH(OCH_3)- group (81.3 d, 60.0 q), (c) a -CH- flanked by a carbonyl group and an amide NH (51.5 d, 4.60 m; "twin" NH doublets 7.97 and 8.10, ratio of 9:1), (d) a second amide NH with an attached CH_2R (45.2 t, NH 6.28 t), (e) an isopropyl group (30.9 d, 22.3 q, 22.2 q), (f) two -CH_2- groups (33.0 t, 28.9 t), and (g) a C_{13} aliphatic linear chain attached to a carbonyl (34.4 t, eight signals at ≈ 29 t, 32.0 t, 25.0 t, 22.8 t, 14.2 q). Preparation of triacetyl bengamide A (3) revealed the location of the three hydroxy groups in 1 because the ^1H NMR signals corresponding to H-5, H-6, and H-7 were shifted downfield in 3 vs. 1 by >1 ppm. The multiplet patterns for these protons in 3 along with a ^1H homo COSY NMR spectrum of 1 clearly revealed the

(3) FAB MS of 1, *m/z* (relative intensity): 585 [$M^+ + H$] (40), 567 [585 – H_2O] (53), 549 [567 – H_2O] (28), 531 [549 – H_2O] (56), 517 [585 + H – C_5H_9] (21), 467 [$M^+ - C_6H_{11}O - H_2O$] (40), 455 [$M^+ + H - C_6H_{11}O - H_2O$] (100), 426 [$M^+ + H - C_8H_{15}O_3$] (57), 381 [$M^+ - C_{10}H_{19}O_4$] (20), 355 [$M^+ + 2H - C_{11}H_{19}O_5$] (99), 310 (25), 229 [$C_{14}H_{28}O_2 + H$] (20). High resolution EIMS, *m/z* (relative intensity): 467.3132 (25), 455.3117 (10), 426.3079 (30), 381.2763 (25), 355.2967 (10), 339.2755 [$M^+ + H - C_{11}H_{20}NO_5$] (10), 257.1125 [$M^+ - C_{14}H_{28}O_2 - C_6H_{11}O$] (33), 228.2084 [$C_{14}H_{28}O_2$] (8), 211.2054 [$C_{14}H_{27}O$] (15), 127.0885 [$C_6H_{11}N_2O$] (28), 126.0804 [$C_6H_{10}N_2O$, see 5] (100), 110.0598 [C_6H_8NO = 126 – NH_2] (12), 109.0523 (C_6H_7NO, see 6] (75). A low resolution EIMS shows the same peaks but with different intensities: 531 (2), 516 (1), 467 (100), 455 (22), 426 (73), 381 (38), 355 (12), 339 (35), 257 (8), 228 (4), 211 (5), 126 (5), 109 (3).

(4) High resolution FAB of bengamide A treated with HCl followed by KCl give an experimental *m/z* at 623 of ±0.0004 vs. that calculated for $C_{31}H_{56}O_8N_2K$.

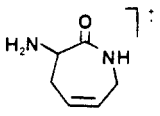
(5) 1: NMR ($CDCl_3$) shifts in ppm from Me_4Si, assignments based on assessing the number of attached protons and the COSY data in Table I; [atom number], ^{13}C δ's at 75 MHz, ^1H δ's and *J*'s at 300 MHz [1], 22.3, 0.99 (d, *J* = 6.9, Me); [2] 30.9, 2.29 (m); [3] 141.9, 5.78 (dd, *J* = 15.5, 6.5); [4] 125.5, 5.44 (dd, *J* = 15.5, 7.3); [5] 74.3, 4.21 (t, *J* = 6), [6] 72.5, 3.60 (bs); [7] 72.8, 3.80 (m); [8] 81.3, 3.80 (m); [9] 172.3; [10] 51.5, 4.60 (m); [11] 28.9, 2.15 (m), 1.75 (m); [12] 33.0, 2.15 (m), 1.95 (m); [13] 70.9, 4.60 (m); [14] 45.2, 3.32 (bm, 2 H); [15] 22.2, 0.99 (d, *J* = 6.9, Me); [16] 173.0; [17] 174.2; [18] 34.4, 2.29 (t, *J* = 7.5, 2 H); [19] 25.0, 1.59 (m, 2 H); [20–27] 29.2–29.7, 1.2–1.4 (bs, 20 H); [28] 32.0; ≈1.3 (m, 2 H); [29] 22.8, ≈ 1.3 (m, 2 H); [30] 14.2, 0.87 (t, *J* = 6.5, Me); [a] 8.10 (d, *J* = 6.3, <10%) 7.97 (d, *J* = 6.3, >90%); [b] 6.28 (t, *J* = 6.3); [OH] 4,27 (bs); [OMe] 60.0, 3.52 (s). $CDCl_3/C_6D_6$ NMR data in Table A, supplementary material.



	R
3	H
4	Me

connectivities shown for C-1 (C-15) to C-8. A regular $^{13}C-^{1}H$ COSY ($CDCl_3$) NMR of **1** supported the assignments for the remaining carbons and their attached hydrogens. Unfortunately, due to sample size limitations, only one significant long range $^{13}C-^{1}H$ COSY NMR correlation was observed for **1**. This correlation between C-8 and the methoxy protons revealed the OMe location as shown. Assignment of C-8 as adjacent to a carbonyl group was based on homo COSY NMR data and chemical shift considerations. At this point, since the polar unit A and the long aliphatic chain B were not part of the ring, four possible structures, **1a–d** could be written. That **1a** was the correct choice could only be established after the completion of the structure proof of bengamide B (**2**), which was facilitated because it was available in larger quantity. Bengamide B (**2**) (viscous oil, $[\alpha]^{20}_{D}$ +34.6° (*c* 0.075, MeOH); IR (neat) 3700–3100, 1740, 1670, 1660 cm^{-1}) displayed NMR[6] data almost identical with that of **1** with the exception of differences due to a N-CH_3 in **2** vs. an N-H in **1**. The tertiary amide methyl (^{1}H NMR: 3.05, s, 3 H; ^{13}C NMR: 36.5, q) must be attached to N-b since the NMR resonance for H-b was missing. The NMR signals corresponding to C-14, H-14, and H-14′ were shifted and the multiplets associated with these protons were simplified in comparison to the corresponding H's of bengamide A. Also, as expected, the molecular formula of bengamide B ($C_{32}H_{58}N_2O_8$) established by FAB MS ($M^+ + H = 599$)[7] differed by a CH_2 vs. that of bengamide A. Preparation of triacetylbengamide B (**4**) and inspection of its NMR parameters along with insights from the COSY NMR spectra of **2** (^{1}H homo and ($^{1}H-^{13}C$)J = 140) substantiated the assignments made for bengamide B. An unambiguous choice in favor of **2a** among possibilities **2a–d** was supported by a $^{1}H-^{13}C$ COSY (J = 9) spectrum containing the key correlations in Table I, which included C-9 to H-7 and H-10, C-16 to H-10 and NMe, and C-17 to H-18, H-18′. Structure **1a** could then be assigned on the basis of its similar spectral properties to **2a**. The proposed structures of **1a** and **2a** are also consistent with the ^{1}H NMR "twin" signals of H-a in both compounds due to two diastereomeric rotamers, in a ratio of 9:1, albeit, as expected, H-b shows only one signal.

Additional spectroscopic and chemical data were obtained to support the above structures. First, a high resolution EIMS of bengamide A[4] showed three fragmentation key peaks which are only compatible with structure **1a**: 228.2084 ($C_{14}H_{28}O_2$, myristic acid, 8%); 126.0804 ($C_6H_{10}N_2O$, **5**, base peak); 109.0523 (C_6H_7NO, **6**, 75%).



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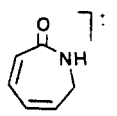

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Second, reduction of **2** (LAH/EtOH/THF) afforded 1-tetradecanol, while basic hydrolysis of **2** (MeOH/KOH 1%) yielded tetradecanoic acid (myristic acid), and myristic acid was also a major component of the crude extract. Repeated attempts to obtain X-ray analysis quality crystals of either bengamide A or simple derivatives have been unsuccessful.

The bengamides can be added to a very short list of other biotoxic natural products known from taxa in the order Choristida.[8] A set of highly antitumor but uncharacterized peptides, geodiastatins, accompanied by another uncharacterized cytotoxin, geodiatoxin 1 have been reported from *Geodia mesotriaena* (family, Geodiidae).[9] Isomalabaricane triterpenes have been reported from *Jaspis stellifera* (family, Jaspidae),[10] and we have found these to be cytotoxic. Also, we recently reported an anthelminthic, antifungal cyclodepsipeptide, jasplakinolide, as a single major component from an undescribed *Jaspis* sp. (family, Jaspidae).[11]

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Supplementary Material Available: Table A containing complete ^{1}H and ^{13}C NMR data of compounds **1**, **2**, **3**, and **4** (3

(6) **2**: NMR ($CDCl_3$) shifts in ppm from Me_4Si, assignments based on assessing the number of attached protons and the COSY data in Table I; [atom number], ^{13}C δ's at 75 MHz, ^{1}H δ's and J's at 300 MHz [1], 22.2, 0.95 (d, J = 6.3, Me); [2] 30.7, 2.26 (m); [3] 141.6, 5.72 (dd, J = 15.6, 6.3); [4] 125.4, 5.40, dd, J = 15.6, 7.1); [5] 74.1, 4.17 (t, J = 6); [6] 72.5, 3.55 (bd, J = 5.1); [7] 72.5, 3.76 (bs); [8] 81.1, 3.76 (bs); [9] 171.8; [10] 51.2, 4.64 (m); [11] 28.9, 2.10 (m), 1.57 (m); [12] 32.6, 2.10 (m), 1.95 (m); [13] 69.1, 4.55 (bt); [14] 53.3, 3.63 (dd, J = 15.0, 9.9), 3.18 (bd, J = 15.0); [15] 0.95 (d, J = 6.3, Me); [16] 171.8; [17] 173.0; [18] 34.3, 2.26 (bt, J = 7.5, 2 H); [19] 24.8, 1.57 (m, 2 H); [20–27] 29.2–29.7, 1.2–1.4 (bs, 20 H); [28] 31.9, ≈1.3 (m, 2 H); [29] 22.6, ≈1.3 (m, 2 H); [30] 14.1, 0.83 (t, J = 7.3, Me); [a] 8.04 (d, J = 6, >90%) 7.92 (d, J = 6, <10%); [OH] 4.27 (bs); [OMe] 59.7, 3.47 (s); [NMe] 36.3, 3.05 (s). CD_3OD NMR data in Table A, supplementary material.

(7) FAB MS of **2**, m/z (relative intensity: 599 [$M^+ + H$] (63), 581 [599 − H_2O] (90), 563 [581 − H_2O] (70), 545 [563 − H_2O] (90), 531 [599 + H − C_5H_8] (60), 481 [$M^+ - C_6H_{11}O - H_2O$] (85), 470 [$M^+ + 2H - C_6H_{11}O - H_2O$] (100), 440 [$M^+ + H - C_8H_{15}O_3$] (10), 395 [$M^+ - C_{10}H_{19}O_4$] (30), 369 [$M^+ + 2H - C_{11}H_{19}O_5$] (85), 324 (30), 229 [$C_{14}H_{28}O_2 + H$] (10).

(8) For a listing of taxa in the Choristida, see: (a) Bergquist, P. R. *Sponges*; University of California Press: Berkeley, 1978; Chapter 5. (b) Bergquist, P. R.; Wells, R. J. In *Marine Natural Products, Chemical and Biological Perspectives*; Scheuer, P. J., Ed.; Academic Press: New York, 1983; Vol. V, Chapter 1.

(9) Pettit, G. R.; Rideout, J. R.; Hasler, J. A. *J. Nat. Prod.* **1981**, *44*, 588.

(10) (a) McCabe, T.; Clardy, J.; Minale, L.; Pizza, C.; Zolio, F.; Riccio, R. *Tetrahedron Lett.* **1982**, *23*, 1982. (b) Ravi, B. N.; Wells, R. J. *Aust. J. Chem.* **1982**, *35*, 39. (c) Ravi, B. N.; Wells, R. J.; Croft, K. D. *J. Org. Chem.* **1981**, *46*, 1998.

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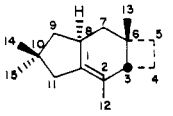
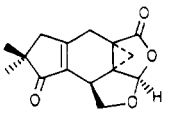
A Stereoselective Electroreductive Cyclization Pathway to the Isolactarane-type Sesquiterpene 1-Sterpurene

Summary: The isolactarane-type sesquiterpene 1-sterpurene (1) was prepared by capitalizing upon a facile electroreductive cyclization that served to convert bisenoate **3** to the trans diester **4a**.

Sir: In 1981, Ayer and co-workers reported the isolation and characterization of several metabolites produced by the fungus *Stereum purpureum*, the causative agent of the so-called silver leaf disease of a variety of trees and scrubs.[1] 1-Sterpurene (1) was isolated from the neutral metabolites and was tentatively assigned the interesting isolactarane-type skeleton shown; it is believed to be the biogenetic precursor of the more highly oxygenated members of the series including, for example, sterepolide (2).[2] The only



1
STERPURENE



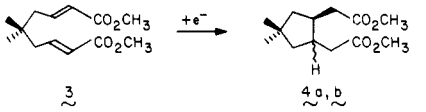
2
STEREPOLIDE

reported synthesis of 1 is that of Murata, Ohtsuka, Shirahama, and Matsumoto, who described the conversion of humulene to 1 under conditions that are believed to be analogous to those involved in its biosynthesis.[3] We now report a total synthesis of 1-sterpurene (1) that makes use of a number of interesting and useful aspects associated with electroreductive cyclization reactions.[4]

One analysis of the problem is illustrated in Scheme I. Key features include the use of an intramolecular electrochemically induced cyclization to convert **3** to **4a**, an acyloin condensation to form the six-membered ring, and a photo [2 + 2] cycloaddition between enone **6a** and ethylene to construct the cyclobutane ring system.

Invariably, cyclization of the bisenoate **3** led to a mixture of trans and cis cyclopentane diesters **4a** and **4b**. In accord with our previous report involving the electroreductive cyclization of an enoate onto an aldehyde or ketone, the trans product dominates over the cis.[4] As illustrated in Table I the trans/cis ratio varied from 2.6:1 to 11.6:1. A priori, the stereochemical outcome appears to be of no consequence to the sterpurene (1) problem since the pro-C_1 carbon in **4** is destined to become sp^2 hybridized. However, as will become apparent, the "natural" propensity toward trans stereoselectivity proved to be beneficial.[5]

Table I

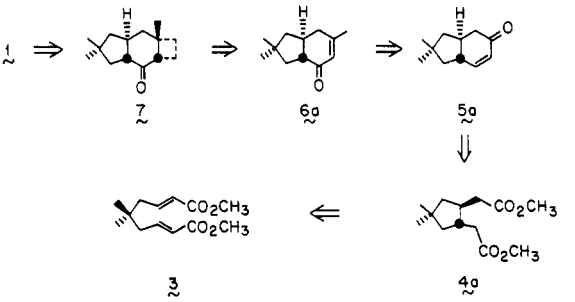


3 4a,b

electrode	proton source	trans/cis ratio	yield (%)
Hg	AcOH, H_2O[a]	2.6:1	82-87
Hg	$CH_2(CO_2Et)_2$[b]	7.5:1	66[c]
glassy carbon	$CH_2(CO_2Et)_2$[b]	7.1:1	73[c]
Cu	$CH_2(CO_2Et)_2$[b]	11.6:1	58[c]

[a] 9:1 CH_3CN/H_2O, 0.9 M Et_4NOTs. [b] CH_3CN, 0.2 M Et_4NOTs. [c] Unoptimized yield.

Scheme I



1 7 6a 5a 3 4a

A Ruhlmann-modified acyloin condensation (4.3 equiv of Na, 4.9 equiv of Me_3SiCl, toluene, reflux, 17 h) served to generate the requisite six-membered ring.[6] However, hydrolysis of the initially formed bis(silyl enol) ether proved problematic. Eventually, it was discovered that heating to 45 °C for 4 h in a mixture of 2:2:1 THF/AcOH/H_2O was most effective, affording the desired acyloin product in 58% yield overall from **4a**. Mesylation (1.5 equiv of MsCl, 1.5 equiv of Et_3N, CH_2Cl_2, -50 to 0 °C) followed by elimination (5 equiv of LiBr, 15 equiv of Li_2CO_3, DMF, reflux 2 h) provided enone **5** in 75% yield, thereby setting the stage for the addition of the pro-C_6 methyl group (1.1 equiv of MeLi, Et_2O, 0 °C to room temperature) and conversion of the resulting tertiary allylic alcohol to enone **6a** (2 equiv of PCC/Celite, CH_2Cl_2, room temperature; 71% from **5**).[7]

While photocycloaddition of ethylene to the trans-fused enone **6a** proceeded smoothly, the cis-fused isomer **6b** proved unreactive under the same conditions (450-W Hanovia, Pyrex, ethylene, -60 to -70 °C). This initially somehwat surprising result can be rationalized by using the Wiesner model for photocycloaddition.[8] Consider, for example, the excited state representations A* and B*, wherein the β-carbon is pyramidal and the methyl substituent is oriented pseudoequatorial. Clearly, the approach of any agent, including a comparatively small molecule of ethylene, should experience an energy raising interaction with the cis-oriented five-membered ring in B*.

As a result of the unreactive nature of **6b**, it proved useless as an intermediate en route to 1-sterpurene (1).

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(3) Trost, B. M.; Chung, J. Y. L. *J. Am. Chem. Soc.* **1985**, *107*, 4586.
(4) Fox, D. P.; Little, R. D.; Baizer, M. M. *J. Org. Chem.* **1985**, *50*, 2202.
(5) See supplementary material paragraph.
(6) Ruhlmann, K. *Synthesis* **1971**, 236.
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