Supplementary Material Available: Complete spectral and analytical data for all new compounds (5 pages). Ordering information is given on any current masthead page.

John T. Welch,* Janet S. Samartino
Department of Chemistry
State University of New York at Albany
Albany, New York 12222

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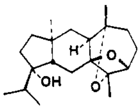
Dictyoxetane, a Novel Diterpene from the Brown Alga *Dictyota dichotoma* from the Indian Ocean

Summary: A specimen of *Dictyota dichotoma* from the Indian Ocean contained dictyoxetane (1), the first example of a new tricyclic diterpene carbon skeleton.

Sir: A study of the brown alga *Dictyota dichotoma* (Hudson) Lamouroux[1] was undertaken as part of a survey of marine organisms from the coast of India. Previous chemical investigations of *Dictyota* species have yielded diterpenes belonging to several different structural classes.[2] Some representative examples are dictyodial from *Dictyota crenulata* and *D. flabellata*,[3] sanadaol from *D. crenulata*,[4] dictyolene from *D. acutiloba*,[5] the dictyols from *D. dichotoma*,[6] the dolabellanes from *D. dichotoma*[6] and *Dictyota* sp.,[7] and the dolastanes from *Dictyota* sp.[8] The Indian Ocean sample of *Dicytota dichotoma* contains at least 20 new diterpenes, most of which belong to the familiar dolabellane class. In this communication we report the structural determination of dictyoxetane (1), the first example of a new tricarbocyclic diterpene skeletal class.



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The sample of *Dictyota dichotoma* was collected by hand at Krusadai Island, Gulf of Mannar, India. The combined chloroform and methanol extracts of *D. dichotoma* were subjected to repeated silica gel chromatography, and the final purification of dictyoxetane (1, $7 \times 10^{-4}\%$ dry weight) was achieved by LC on μ-Porasil using 8:1 hexane–ethyl acetate as eluant.

Dictyoxetane (1), $[\alpha]_D$ +35.0° (*c* 3.0, $CHCl_3$) is a colorless crystalline solid, mp 87–90 °C, that has the molecular formula $C_{20}H_{32}O_3$. The IR spectrum contained a weak hydroxyl band at 3600 cm^{-1} but no carbonyl bands. Five signals at δ 80.1 (s), 80.6 (s), 81.3 (d), 82.7 (s), and 97.2 (s) in the ^{13}C NMR spectrum were assigned to carbon atoms bearing oxygen. Since there were no signals at δ >100 in the ^{13}C NMR spectrum, we concluded that dictyoxetane (1) must be a tricarbocyclic diterpene with two ether rings. The ^{1}H NMR spectrum contained signals at δ 0.91 (d, 3 H, J = 6.5 Hz) and 0.97 (d, 3 H, J = 6.5 Hz), assigned to an isopropyl residue, three methyl signals at δ 1.10 (s, 3 H), 1.30 (s, 3 H), 1.37 (s, 3 H), and a C*H*OR signal at δ 4.40 (br d, 1 H, J = 3 Hz). Even assuming that the structure of dictyoxetane could be derived by further cyclization of the dolabellane ring system, there were too many possibilities for the compound to be identified by analysis of spectral data alone. The structure of dictyoxetane (1) was therefore determined by a single-crystal X-ray analysis.

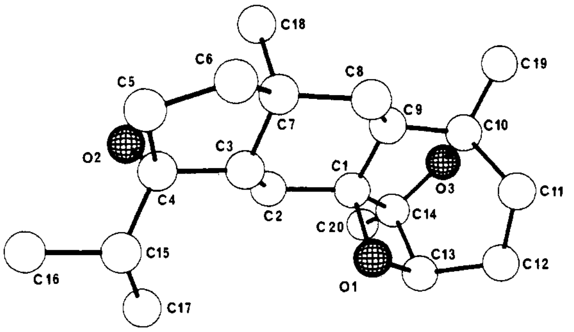

Figure 1. A computer-generated perspective drawing of the final X-ray model of dictyoxetane (1). Hydrogens are omitted for clarity, and no absolute configuration is implied.

Crystals of dictyoxetane (1) belonged to the monoclinic crystal class with $a = 7.842$ (2) Å, $b = 16.320$ (4) Å, $c = 8.242$ (1) Å, and $\beta = 115.86$ (2)°. Systematic extinctions indicated space group $P2_1$ with one molecule of $C_{20}H_{32}O_3$ forming the asymmetric unit. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a computer-controlled four-circle diffractometer using variable speed, 1° ω-scans, and graphite monochromated Cu $K\bar{\alpha}$ radiation (1.54178 Å). Of the 1331 reflections measured in this way, 981 (74%) were judged observed ($F_o \geq 3\sigma(F_o)$) after correction for Lorentz, polarization, and background effects.[9] A phasing model was found by using the MULTAN series of programs,[9] and the first E synthesis revealed most of the non-hydrogen atoms. The remaining non-hydrogen atoms were located with tangent formula recycling,[10] and hydrogen atoms were located on a subsequent ΔF synthesis. Block diagonal least-squares refinements with anisotropic non-hydrogen atoms and isotropic hydrogens have converged to a conventional crystallographic residual of 0.074 for the observed reflections. Additional crystallographic details can be found in the supplementary material.

Figure 1 is a computer-generated perspective drawing of the final X-ray model less hydrogens. The absolute configuration shown is an arbitrary choice. The five-membered ring has an envelope conformation with C7 serving as the flap. The six-membered ring is in a chair conformation as is the seven-membered ring. The oxetane ring is only slightly folded with all of the torsional angles roughly ±6°. The C–O interatomic distances are 1.50 (1)

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[1] A voucher specimen (Herbarium #M.A.-64) was deposited in the Central Marine Fisheries Research Institute, Mandapan Camp, India.

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[9] All crystallographic calculations were done on a PRIME 850 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were: REDUCE and UNIQUE, data reduction programs by M. E. Leonowicz, Cornell University, 1978; MULTAN 78, MULTAN 80, and RANTAN 80, systems of computer programs for the automatic solution of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson Syntheses) written by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1978 and 1980; DIRDIF written by P. T. Beurskens et al., University of Nijmegan, the Netherlands, 1981; MITHRIL, an automatic solution package written by C. J. Gilmore, University of Glasgow, Scotland, 1983; BLS78A, an anisotropic block diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, a crystallographic illustration program by W. D. S. Motherwell, Cambridge Crystallographic Data Centre, 1978; BOND, a program to calculate molecular parameters and prepare tables written by K. Hirotsu, Cornell University, 1978.

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Å [O1–C1] and 1.48 (1) Å [C13–O1], and the C–C distances are 1.55 (1) Å [C1–C14] and 1.57 (2) Å [C13–C14].

The dictyoxetane carbon skeleton has not been reported previously. Since dictyoxetane (1) cooccurs with dolabellanes in *Dictyota dichotoma*, it is most likely formed by 3,9-cyclization of a "dolabellane" precursor. The structures of the dolabellanes from this collection of *D. dichotoma* will be reported in the near future.[11]

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Supplementary Material Available: Tables of fractional coordinates, thermal parameters, interatomic distances, and interatomic angles for dictyoxetane (1) (5 pages). Ordering information is given on any current masthead page.

K. C. Pullaiah, R. K. Surapaneni
C. Bheemasankara Rao*
Department of Chemistry
Andhra Univeristy
Visakhapatnam 530 003, India

Kim F. Albizati, Brian W. Sullivan
D. John Faulkner*
Scripps Institution of Oceanography
University of California, San Diego
La Jolla, California 92093

He Cun-heng, Jon Clardy*
Department of Chemistry—Baker Laboratory
Cornell University
Ithaca, New York 14853-1301

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Silylstannanes: Useful Reagents for Bis Functionalization of α,β-Unsaturated Ketones and Acetylenes[†]

Summary: A series of silylstannanes have been prepared for use in the difunctionalization of organic molecules.

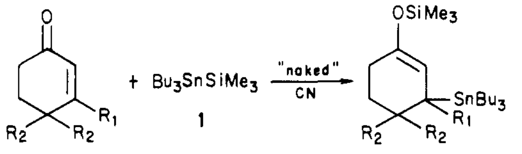
Sir: Synthetic methodology based on the use of silylated and stannylated reagents has grown explosively in the last few years. Both the Si–C and Sn–C bonds are capable of undergoing a variety of useful transformations,[1] yet unprovoked these moieties possess good stability. We have begun a program to examine the chemistry of silylstannanes as reagents which could allow the introduction of both silicon and tin directly into organic substrates. Subsequent individual manipulation of the silicon and tin groups could provide powerful new synthetic methods. This report describes our initial results in the silylstannylation of α,β-unsaturated ketones and acetylenes.

Silylstannanes 1 with methyl, butyl, and phenyl substituents have been known for some time;[2] however, the literature concerning their organic chemistry is sparse.[3] We have prepared a series of silylstannanes using several of the standard procedures.[2] For large-scale synthesis the Still preparation of R_3SnLi[1b] from the corresponding hydride and LDA followed by quenching with a silyl chloride is the method of choice (eq 1).[4]

$$R_3SnH \xrightarrow[(2)\ R^1_3SiCl]{(1)\ LDA} R_3SnSiR^1_3 \qquad (1)$$

$$R_3 = Me_3,\ Bu_3,\ Ph_3;\ R^1_3 = Me_3,\ Et_3,\ t\text{-}BuMe_2$$

The first attempts to add 1 ($R_3 = Bu_3$; $R^1_3 = Me_3$) to cyclohexenone in the presence of Lewis acids[5] ($BF_3{\cdot}Et_2O$, $Ti(O\text{-}i\text{-}Pr)_4$, $Me_3SiOSO_2CF_3$) were unsuccessful; however, the use of "naked" cyanide ion catalysis (KCN/18-crown-6,[6] Bu_4NCN, TASCN[7]) efficiently catalyzed an exothermic Michael addition to produce **2a** in high yield (eq 2).[8] The moisture-sensitive product was isolated by distillation directly from the reaction vessel.[9,10] We later found that potassium *tert*-butoxide also catalyzed the addition reaction albeit in lower yield (~45% conversion after 72 h). Somewhat surprising was the observation that this reaction was not catalyzed by fluoride ion.[11]



(2)

2a, $R_1 = R_2 = H$ (75%)
b, $R_1 = Me$; $R_2 = H$ (77%)
c, $R_1 = H$; $R_2 = Me$ (68%)

We have briefly examined the scope of this reaction and find it to be sensitive to steric bulk on the silicon atom. Thus while Me_3Si, $PhMe_2Si$, and n-$BuMe_2Si$ groups all participate in the Michael addition, the Et_3Si and t-$BuMe_2Si$ groups prevent the reaction. In contrast, steric bulk on tin is apparently of little consequence as both

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[1] (a) For a general review of the functional group transformations of silanes, see: Colvin, E. "Silicon in Organic Synthesis"; Butterworths: New York, 1981. (b) For leading references to the transformations of organotin compounds, see: Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481-1487; **1977**, *99*, 4836-4838.

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[8] Still has prepared compounds analogous to 2 by conjugate addition of Bu_3SnLi to enones and trapping the intermediate with trimethylsilyl chloride. See ref 1b and: Still, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 2493-2495.

[9] All new compounds gave acceptable elemental analyses (C ± 0.27, H ± 0.33) and/or high-resolution mass spectral analyses.

[10] General procedure: The enone (30 mmol) and (trimethylsilyl)tributylstannane (30 mmol) were combined in a dry flask with magnetic stirrer under a nitrogen atmosphere. Tetrabutylammonium cyanide (50 mg, 0.06 mmol) was added, and a mildly exothermic reaction began immediately. When the exotherm subsided, the mixture was warmed to 40 °C until the reaction was complete by GLC analysis (4-15 h). The product was distilled directly from the reaction vessel as a clear colorless oil.

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