on the basis of the hydrolysis kinetics of authentic 13 (X = H).

**Relevance of 7 and 12 to the Mechanism of DNA Strand Scission by BLM.** While the model hydroperoxide 7 mimics the BLM-DNA reaction in its ability to produce base propenal in neutral solution, a closer examination of this compound reveals that it may not provide an appropriate model for the putative DNA hydroperoxide 3. The results of the present study indicate that the observed breakdown of 7 is initiated by a rearrangement to the perester 9, which polarizes the O-O bond sufficiently to enable heterolytic cleavage. Although one might speculate that the postulated DNA hydroperoxide 3 could be similarly activated by an internal migration of the 3'-phosphoryl group, this would require scission of the (3')-P-O bond, inconsistent with our previous oxygen labeling studies, which have established that this bond remains intact.[33]

Thus, it appears that perester formation in the model system is an undesirable artifact due to the unfortunate choice of a 3' blocking group. A more appropriate model of 3 would be a 4'-hydroperoxynucleoside with a 3' substituent unable to migrate. From this point of view, 8 would provide a suitable model since, for stereochemical reasons, it does not rearrange to a perester. In aqueous solution, 8 decays at a very slow rate ($t_{1/2}$ = several hours) and does not give rise to either thymine propenal or MDA (data not shown). This observation strongly suggests that the introduction of a hydroperoxy group at C4' alone may not be sufficient to account for the cleavage of DNA, which is observed in the presence of activated BLM. Since this calls into question an independent role of 3 in the cleavage of the C3'-C4' bond of DNA (Figure 2), one might consider the possibility that this process is mediated by further intervention of the Fe-BLM complex beyond its initial role in radical formation at C-4'. It is not unreasonable to assume that the drug remains in close proximity to the initial lesion for a significant period and provides the necessary catalysis for a Criegee rearrangement in 3 by acting as a Lewis acid.[11]

Burger and co-workers demonstrated that the formation of base propenals from DNA by activated BLM is a relatively slow process, resolvable kinetically from the more rapid strand cleaving event.[29] Although the intermediate propenal precursor could be coprecipitated with the DNA following strand scission, its exact structure has not been determined. Compound 12 provided an opportunity to evaluate the possibility that Burger's intermediate corresponds to the aldehyde 5 (Figure 2). In several respects, 12 does resemble the species described by Burger et al.[29] At 4 °C in pH 7 buffer, 12 decomposes to give thymine propenal at a rate of 0.03 $min^{-1}$, which is essentially identical with the reported rate of 0.02 $min^{-1}$ in DNA under the same conditions. The breakdown of 12, however, differs from that of the DNA intermediate in that thymine and MDA are also formed in substantial quantities. Extensive investigations undertaken in our laboratory indicate that base release from DNA occurs predominantly through pathway B (Figure 1) and is not accompanied by MDA.[13] We have, however, found the observed thymine/thymine propenal ratio from 12 to be very sensitive to a variety of factors including pH (Figure 6), temperature, solvent composition, and ionic strength (data not shown). Given that these physical changes can dramatically alter the product distribution in 12, we would not rule out the possibility that the generation of its equivalent (5) in the constrained environment of a DNA polymer might favor the formation of base propenals exclusively. Experiments are underway in order to resolve this discrepancy between the natural and model systems.

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## Naurol A and B, Novel Triterpene Alcohols from a Pacific Sponge

Florecita S. De Guzman and Francis J. Schmitz*

*Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73019-0370*

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Two new stereoisomeric triterpene alcohols with an uncommon symmetrical carbon skeleton centered about a linear conjugated tetraene moiety and having only two carbocyclic rings have been isolated from a sponge from Nauru. The structures were determined primarily from $^1H$ and $^{13}C$ NMR data. Both alcohols are mildly cytotoxic to murine leukemia cells (P388).

Although triterpenes of varied skeletal arrangements are abundant among terrestrial plant products,[1] they are far less prominent among secondary metabolites reported to date from marine organisms.[2] The majority of all triterpenes reported have the conventional skeletons arising from cyclization of 2,3-squalene epoxide to fused polycyclic products. More unusual are incompletely cyclized compounds or ones exhibiting cyclization within the chain rather than with cyclizations beginning at one end. In our continuing search for bioactive compounds from marine organisms we have isolated two stereoisomeric triterpene alcohols that have a novel, partially cyclized skeleton which has been noted in only one other natural product.[3] The new compounds display cytotoxicity against murine lymphocytic leukemia.

The new triterpenes were isolated from several sponge specimens collected at Nauru Is. These specimens looked superficially the same and hence were extracted together, but, unfortunately, subsequent taxonomic analysis revealed that the collection was a mixture of a *Rhaphisia* sp. (order

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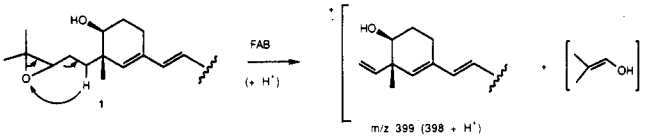
Poecilosclerida, family Tedaniidae) and another sponge classified only as belonging in the order Axinellida, family Euryponidae. Hence the exact origin of the new products cannot be specified at this time.

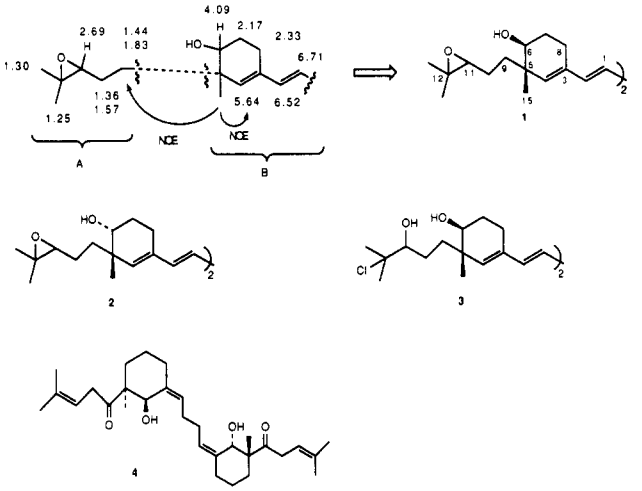
The new alcohols were isolated by solvent partitioning followed by chromatography over normal and reverse phase, see experimental. The APT[4] spectrum of naurol A (1) showed signals for only 15 carbons and 22 nonexchangeable protons. A signal integrating for one additional exchangeable proton was observed in the proton NMR spectrum. The presence of 2–3 oxygen atoms was inferred from the presence of three carbon NMR signals in the region of 58.7–64.5 ppm, and these combined data pointed to a formula of $C_{15}H_{23}O_{2-3}$. However, the FAB mass spectrum (dithiothreitol/dithioerythritol matrix) showed its highest mass ion at $m/z$ 399. FAB MS using added




$Li^+$ gave a highest mass ion at 405 (m + $Li^+$) and with added $Na^+$ at 421 (m + $Na^+$). This suggested that naurol A was much larger than the $^{13}C$ NMR data implied, and hence a symmetrical molecule with the formula $C_{30}H_{46}O_{4-6}$ was considered, although the molecular weight for this formula exceeds that of $m/z$ 399. The infrared spectrum supported the presence of hydroxyl group(s) ($3450^{-1}$ cm). The UV spectrum exhibited $\lambda_{max}$ at 286 nm (49 131) and since the presence of carbonyl groups was ruled out by the lack of relevant IR and $^{13}C$ NMR absorptions, naurol A must have a conjugated tetraene moiety based on calculations from Woodward's rules.

The presence of a terminal dimethyl epoxide group in 1 was inferred from the correlations noted in a H/H COSY spectrum between a methine proton signal at 2.69 ppm and broad singlet methyl signals at 1.25 and 1.30 ppm. This was supported by the associated carbon signals determined by HETCOR at 19.0, 25.2, and 64.5 ppm plus a quaternary carbon signal at 58.7 ppm. These shifts are characteristic of terminal dimethyl epoxides.[5] The methine proton signal at 2.69 ppm was also coupled with methylene proton signals at 1.36 and 1.57 ppm, which in turn were coupled to another pair of methylene proton resonances at 1.44 and 1.83 ppm. No further coupling to this latter set of methylene protons was noted. This established partial structure A and confirmed that it must be attached to a quaternary carbon.

Partial structure B was also deduced from NMR data. A 13-Hz coupling between the vicinal olefinic protons (see partial structure B) suggested that they were trans oriented, and in the COSY plot both these protons were correlated with a third olefinic proton absorbing at 5.64 ppm. Evaluation of the COSY plot and decoupling experiments confirmed the spin sequence from 5.64 ppm through the two methylene groups to the carbinol methine signal at 4.09 ppm. The relative assignments of the vicinal olefinic proton signals at 6.52 and 6.71 ppm could not be made on the basis of any difference in the size of coupling constants with the 5.64 ppm signal, but these assignments were resolved by HETCOR[6] and INAPT[7] experiments.




Irradiation of the 5.64 ppm proton signal in an INAPT experiment (2/3-bond couplings) produced a carbon signal at 136.6 ppm which a HETCOR experiment confirmed was one-bond coupled to the 6.52 ppm proton signal. Hence, the 6.52 proton signal is due to H-2. The other signal evident in this INAPT spectrum was at 63.8 ppm, revealing 3-bond coupling between H-4 (5.64 ppm) and the carbinol carbon. Irradiation of the quaternary methyl signal at 1.13 induced NOE's on the H-4 and H-9 signals (3.9, 5.2%). Hence this quaternary methyl and the associated quaternary carbon must be connected to complete the substituted cyclohexenol structure of partial formula B.

The combined partial structure A–B accounts for all of the formula elements detected by $^1H$ and $^{13}C$ NMR, $C_{15}H_{23}O_2$. Doubling of this partial structure gives the symmetrical dimeric structure 1 that we propose for naurol A. The conjugated tetraene moiety of 1 is consistent with the observed UV absorption, 286 nm (calculated by Woodward's rules, 294 nm). However, the molecular weight of 1, 470 amu, is 72 amu greater than that of the highest mass ion observed in FAB mass spectra. This discrepancy can be accounted for by assuming that naurol A undergoes facile cleavage between the C-10/11 bonds with stabilization of the cation by ring formation with the alcohol oxygen. Alternatively, the highest mass ions observed in the FAB mass spectra [$m/z$ 399 = 398 + $H^+$; 405 = 398 + $Li^+$; 421 = 398 + $Na^+$] could arise via an "outside McLafferty" rearrangement[8] shown below on the protonated [or metal complexed] molecule.

The carbinol proton in 1 is assigned a pseudoaxial orientation based on its distinct coupling constants of 4 and 10 Hz. Absence of any NOE between this carbinol proton and the quaternary methyl indicated a trans relationship between these groups to give the overall relative stereochemistry shown in formula 1 (see also corroborative evidence below).

Comparison of the $^1H$ and $^{13}C$ NMR data for naurol A and B, see Table I, revealed that the two had nearly identical structures. Decoupling experiments, COSY data, and an INAPT experiment (irr. at 5.64 ppm, induced signals at 136.6, 58.1, and 25.3 ppm) confirmed that the two compounds had the same overall skeleton and double bond geometry and likely differed only in stereochemistry at the carbinol carbon.

Indeed, the most significant difference in the spectral data of these two compounds is found in the NMR chemical shifts of the carbinol carbons and protons (see C-6 and H-6 in Table I). The carbinol proton (H-6) signal of naurol

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(5) Cf.: Groweiss, A.; Kashman, Y. *Tetrahedron* **1983**, *39*, 3385. Poet, S. E.; Ravi, B. N. *Aust. J. Chem.* **1982**, *35*, 77.
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Table I. $^1H$ and $^{13}C$ NMR Data for 1–3[a]

| | 1 | | | | 2 | | | | 3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C* | δ $^{13}C$ | δ $^1H$ | mult | J, Hz | δ $^{13}C$ | δ $^1H$ | mult | J, Hz | δ $^{13}C$ | δ $^1H$ | mult | J, Hz |
| 1 | 130.1 | 6.71 | d | 13.2 | 129.8 | 6.68 | d | 13.3 | 129.7 | 6.72 | d | 13.0 |
| 2 | 136.9 | 6.52 | d | 13.2 | 136.6 | 6.49 | d | 13.3 | 136.7 | 6.53 | d | 13.0 |
| 3 | 133.0 | | | | 132.7 | | | | 132.5 | | | |
| 4 | 141.0 | 5.64 | br s | | 140.0 | 5.64 | s | | 140.9 | 5.67 | br s | |
| 5 | 41.4 | | | | 40.9 | | | | 41.2 | | | |
| 6 | 63.8 | 4.09 | d | 10, 4 | 58.1 | 4.23 | m | | 63.7 | 4.09 | d | 10.4, 6.2 |
| 7 | 28.9 | 2.17 | m | | 29.7 | 2.28 | m | | 29.3 | 2.16 | m | |
| 8 | 24.9 | 2.33 | m | | 25.3 | 2.30 | m | | 26.1 | 2.34 | m | |
| 9 | 36.8 | 1.83, 1.44 | m | | 37.2 | 1.80, 1.44 | m | | 37.2 | 2.02, 1.56 | m | |
| 10 | 24.2 | 1.57, 1.36 | m | | 23.8 | 1.57, 1.32 | m | | 28.6 | 1.46, 1.37 | m | |
| 11 | 64.5 | 2.69 | m | | 64.1 | 2.67 | t | | 79.6 | 3.44 | d | 7.8, 2.6 |
| 12 | 58.7 | | | | 58.7 | | | | 76.1 | | | |
| 13 | 25.2 | 1.30 | s | | 24.8 | 1.28 | s | | 27.3 | 1.59 | s | |
| 14 | 19.0 | 1.25 | s | | 18.6 | 1.28 | s | | 22.7 | 1.56 | s | |
| 15 | 23.0 | 1.13 | s | | 24.3 | 1.10 | s | | 24.6 | 1.13 | s | |

[a] $CDCl_3$, 300 MHz for $^1H$ and 75.4 MHz for $^{13}C$.

B appears at 4.23 ppm as an unresolved multiplet of ~24 Hz width. Furthermore, an NOE was detected between H-6 and the quaternary methyl signal (1.10 ppm), confirming that these groups are cis to one another as shown in structure **2**. Observation of this NOE strengthens the conclusions drawn above from the *absence* of any NOE between these protons in naurol A.

The width of the H-6 proton signal suggests that **2** adopts a conformation with both the OH and quaternary methyl groups in pseudoequatorial positions and the carbinol proton pseudoaxially disposed. This conformation should be more stable than the alternate one with both the OH and the quaternary methyl groups in pseudoaxial positions. However, the unresolved, broad nature of the H-6 signal suggests facile interconversion between the two more extreme possible conformers.

From a portion of crude extract that was stored in chloroform solution for 7 months, a very small amount of a third naurol-type of compound was isolated in addition to naurol A and B. Since this material was not isolated from extracts that were processed promptly, the third naurol product is suspected to be an artifact arising from reaction of naurol A with HCl in the solvent. Decoupling experiments and the $^1H$ and $^{13}C$ NMR data in Table I confirmed that the structure of the trace metabolite was identical with that of naurol A, except for the terminal epoxide. The downfield shift of H-11 (3.44 ppm), methyl-13 and methyl-14 (1.59, 1.53 ppm) in the artifact relative to those signals in naurol A, see Table I, suggested that the epoxide was not intact in the former. The presence of an additional exchangeable proton at 1.52 ppm and the proton and carbon chemical shifts for H-/C-11 (3.44/79.6 ppm) indicated that there was a hydroxyl group at this position. The proton chemical shifts of methyl-13 and methyl-14 are farther downfield than those of 1,1-dimethyl-1,2-diol systems (~1.17, 1.22)[9] but are very consistent with shifts reported for methyl groups in $(CH_3)_2$-ClCCH(OH) moieties (~1.57 ppm).[10] Hence we propose structure **3** for this artifact even though mass spectral analysis failed to show a molecular ion peak to corroborate the presence of chloride.

Naurol A and B are toxic to murine lymphocytic leukemia cells: P388, $ED_{50}$ 4.6 and 4.4 μg/mL, respectively (average of two analyses for each).[12]

The unusual partially cyclized squalene skeleton present in naurol A and B has been reported in only one other natural product, limatulone (**4**). Limatulone was isolated from a limpet, *Collisella limatula*,[3] and it is interesting that these very uncommon, skeletally related triterpenes have been found in such different sources. This suggests that the ultimate source of these products may be a microorganism of some type, e.g. alga, bacterium, or fungus.

## Experimental Section

Flash chromatography columns were made using Merck silica gel 60H. Alltech Econosphere C18 5μ 10 mm × 29.9 cm and Alltech Econosphere silica 5μ 10 mm × 30 cm columns were used in the HPLC separations. All solvents used in the extraction and separations were distilled prior to use.

**Extraction and Isolation Procedures.** The sponge was collected from the waters surrounding the island of Nauru in the western Pacific in 1985 and was frozen shortly after collection. A portion of the frozen organism (471.71 g) was thawed, cut into very small pieces, and then soaked in methanol (500 mL) for 1 day and then twice more in methanol–chloroform (1:1) for 1 day each. The methanol extract and the first chloroform–methanol extract were combined and concentrated to give 24.65 g of crude extract. This extract was partitioned between dichloromethane and water. The dichloromethane layer was concentrated to give 2.34 g of material, which was then partitioned between hexane and 10% aqueous methanol. The hexane layer was concentrated to give 1.86 g of material which was then subjected to flash chromatography.

The second methanol–chloroform extract was concentrated to give 5.67 g of crude extract, which was stored in chloroform at 0 °C for 7 months. The crude extract was then evaporated to dryness and partitioned between dichloromethane and water. The dichloromethane layer was concentrated to give 0.5249 g of material, which was then partitioned between hexane and 10% aqueous methanol. The hexane layer was concentrated to give 0.43 g of material, which was subjected to silica gel flash chromatography and HPLC on silica gel, in a manner very similar to that described above, with a final separation on C-18 reverse-phase HPLC (20% aqueous MeOH) to give **1**, **2**, and **3** in that order.

The second portion of the frozen sponge (276.93 g) was soaked in methanol (500 mL) for 1 day, in methanol–chloroform (1:1, 500 mL) for 5 h, and again in methanol–chloroform (1:1, 500 mL) for 1 day. The methanol and methanol–chloroform extracts were combined to give 20.34 g of crude extract after removal of solvents.

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(10) Cf: Ahond, A.; Bowden, B. F.; Coll, J. C.; Fourneron, J. D.; Mitchell, S. A. *Aust. J. Chem.* **1981**, *34*, 2657.

(11) Patra, A.; Chang, C. W. J.; Scheuer, P. J.; Van Duyne, G. D.; Matsumoto, G. K.; Clardy, J. *J. Am. Chem. Soc.* **1984**, *106*, 7981.

(12) Gueran, R. I.; Greenberg, N. H.; Macdonald, M. M.; Schumacher, A. M.; Abbot, B. J. *Cancer Chemother. Rep., Part 3* **1972**, *3*(2), 1. 1. Effective doses ($ED_{50}$) in the tissue culture tests are expressed as concentrations in micrograms/milliliter of test material in the growth medium that causes 50% inhibition of cell growth. "Active" materials display an $ED_{50}$ <10 μg/mL. PS (P388) refers to in vitro lymphocytic leukemia.

A part of this crude extract (6.51 g) was partitioned between dichloromethane and water. The dichloromethane layer, upon concentration, gave 1.52 g of material, which was then partitioned between hexane and 10% aqueous methanol. The hexane layer was concentrated to give 1.33 g of material which was subjected to flash chromatography, HPLC on silica gel, and reverse-phase HPLC in nearly the same manner as described above to give more naurol A and B.

From the combined separations 505 mg of naurol A (1), 61.4 mg of naurol B (2), and 10.1 mg of 3 were obtained.

**Naurol A (1)**: white solid; mp 97 °C; $[\alpha]$ = +6.21° ($c$ = 2.64, MeOH); UV $\lambda_{max}$ 286 nm ($\epsilon_{max}$ 49 131); IR (thin film) 3416 $cm^{-1}$; $^1H$ NMR, see Table I; $^{13}C$ NMR, see Table I; LRMS (12 eV) $m/z$ (relative intensity) 314.1 (10.3), 278.0 (26.1), 228.0 (10.2), 214.0 (25.5), 192.1 (18.2), 180.0 (45.8), 177.8 (100.0), 164.0 (16.7), 84.8 (91.6), 82.9 (98.9); FAB MS with added $Na^+$ $(m + Na)^+$ 421; FAB MS $(m + H)^+$ 399; FAB MS with added $Li^+$ $(m + Li)^+$ 405.

**Naurol B (2)**: white solid; $[\alpha]$ = +12.63° ($c$ = 0.19, MeOH); UV $\lambda_{max}$ 292.4 nm ($\epsilon_{max}$ 44 236); IR (neat) 3466 $cm^{-1}$; $^1H$ NMR see Table I; $^{13}C$ NMR, see Table I; LRMS (12 eV) $m/v$ (relative intensity) 314.1 (5.8), 278.0 (10.3), 228.0 (7.9), 213.9 (12.0), 192.0 (11.9), 180.0 (38.5), 177.9 (100.0), 164.0 (12.6), 85.0 (46.3), 83.0 (56.9).

**Compound 3**: white film; $^1H$ NMR, see Table I; $^{13}C$ NMR, see Table I; LRMS (70 eV) $m/z$ (relative intensity) 389.1 (11.3), 387.1 (23.4), 385.1 (17.3), 314.0 (12.0), 214.0 (16.9), 179.9 (38.1), 177.9 (100.0).

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**Registry No.** 1, 130246-98-9; 2, 130322-42-8.

**Supplementary Material Available:** $^1H$ and $^{13}C$ NMR spectra of naurol A and B (4 pages). Ordering information is given on any current masthead page.

# Sterols of Marine Invertebrates. 63.[1] Isolation and Structure Elucidation of Sutinasterol, the Major Sterol of the Marine Sponge *Xestospongia* sp.

Russell G. Kerr,[†] Sutinah L. Kerr,[†] George R. Pettit,[‡] Delbert L. Herald,[‡] Thomas L. Groy,[‡] and Carl Djerassi*,[§]

*Hopkins Marine Station, Stanford University, Pacific Grove, California 93950, Cancer Research Institute and Department of Chemistry, Arizona State University, Tempe, Arizona 85287, and Department of Chemistry, Stanford University, Stanford, California 94305*

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A new sterol, sutinasterol ((24*R*)-24-ethyl-26,26-dimethyl-3β-hydroxycholesta-7,25(27)-diene) with a side chain arising from quadruple biomethylation has been isolated from the marine sponge *Xestospongia* sp. Since it represents the bulk (94%) of the sterol fraction, it presumably plays a biological role in membrane function. Four minor sterols were also characterized, one of which appears to be a biosynthetic intermediate of sutinasterol. A second trace sterol contains a side chain that is the result of five biomethylations and is the largest sterol isolated from natural sources to date. The structures of these sterols were deduced from spectral data ($^1H$ and $^{13}C$ NMR and MS). A crystal structure study of sutinasterol was performed to determine the stereochemistry of the $C_{24}$ ethyl group.

## Introduction

The occurrence of a wide variety of novel sterols in sponges has been well documented.[2] This includes unconventional sterol nuclei as well as sterol side chains with cyclopropanes, cyclopropenes, and ones with high degrees of alkylation. Recently, the main emphasis in our laboratory has been on elucidating the biosynthesis of these compounds.[3] It is most interesting to examine unusual sterols that are present in large quantities, as these very likely play a functional (rather than metabolic) role in cell membranes.[4] Unconventional sterols often co-occur with conventional ones and are sometimes present in small amounts.[2] It is therefore particularly interesting when a sponge is found with an unusual sterol as the overwhelmingly predominant one.

Analysis of a demosponge, *Xestospongia* sp., from Puerto Rico showed that one sterol, designated sutinasterol, composed 94% of the sterol mixture. Sutinasterol has not previously been isolated and was shown by MS analysis to have a $C_{12}$ side chain, presumably the product of quadruple bioalkylation. This information, coupled with $^1H$ and $^{13}C$ NMR analysis, suggested that sutinasterol had the structure shown in Figure 1. An X-ray crystal structure study was performed to confirm this structure

[†] Hopkins Marine Station, Stanford University.
[‡] Arizona State University.
[§] Department of Chemistry, Stanford University.

(1) For part 62 in this series, see: Tam Ha, T. B.; Djerassi, C. *Steroids* **1989**, *53*, 356.

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