Tetrahedron Vol. 37, No. 15, pp. 2569 to 2573, 1981
Printed in Great Britain.

0040–4020/81/152569–05$02.00/0
Pergamon Press Ltd.

NEOLEMNANE AND EREMOPHILANE SESQUITERPENOIDS FROM THE PACIFIC SOFT CORAL *LEMNALIA AFRICANA*

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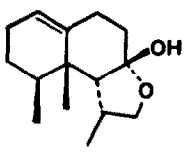
(*Received in U.S.A.* 17 *March* 1981)

Abstract—Two new sesquiterpenoids of the unprecedented neolemnane ring system, and one eremophilane-derived sesquiterpene diol have been isolated from the pacific soft-coral *Lemnalia africana*. The structure of the novel neolemnane compounds, **4** and **5**, were confirmed by X-ray crystallography, and the diol, **6**, has been described based upon spectral analysis and chemical modification.

The widely-distributed Pacific soft-coral *Lemnalia africana* May (Octocorallia, Alcyonaceae) is known to produce mainly sesquiterpenoids of the nardosinane type, typified by 2-desoxylemnacarnol (**1**).[1] Two other compounds, africanol (**2**)[2,3] and the diol **3**,[4] represent additional structure types isolated from this source. We wish to report here the structures of three new sesquiterpenoids, **4**, **5** and **6**, isolated from *L. africana* collected in Palau, Western Caroline Islands. The ketones **4** and **5** possess new and irregular terpenoid structures for which we suggest the semisystematic name neolemnane.[5] These latter compounds and the diol **6**, an eremophilane derivative, represent an extension of the biosynthetic capability of soft-corals from this genus.



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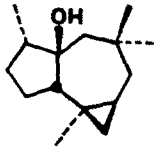

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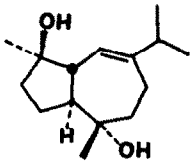

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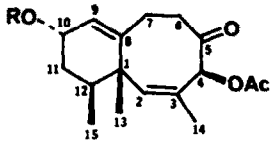
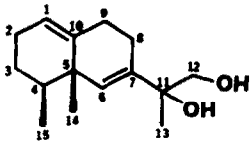


4, R = H
5, R = Ac



6

The sesquiterpenoids **4–6** were obtained by repeated column and high performance liquid chromatography (hplc) of the $CHCl_3$/MeOH extract of *Lemnalia africana*.[8] The hydroxyketone **4** was found as the major terpenoid component (3.0% extract), while the corresponding acetate **5**, and the unrelated diol **6**, were less concentrated (0.15% and 0.6% of the extract, respectively). This collection of *L. africana* did not contain compounds **1–3**, but it did contain two germacrene derivatives which will be described in a separate paper.

The hydroxyketone **4** crystallized from one h.p.l.c. fraction, m.p. 111–112°, and analysed for $C_{17}H_{24}O_4$ by high-resolution mass and ^{13}C NMR spectrometry (Table 1). IR absorptions at 3600, 1739 and 1715 cm^{-1}, coupled with ^{13}C NMR bands at 63.5 (d), 170.4 (s), 20.5 (q) and 190.8 (s) ppm, indicated the four O atoms in **4** to be composed of OH, OAc and CO functionalities. The ^{13}C NMR spectrum of **4** also indicated two double bonds to be present, therefore establishing this compound as a bicyclic hydroxyketone of probable sesquiterpenoid origin.

The 220 MHz ^1H NMR spectrum of **4**, with appropriate spin-decoupling experiments, gave considerable information concerning the locations of these aforementioned substituents. Immediately obvious was the existence of only three Me groups (or vestiges) associated with the bicarbocyclic skeleton, a vinyl Me at δ 1.68, a bridgehead methyl at δ 1.01, and a secondary Me at δ 0.98 (d, $J = 6.8$ Hz). These data were inconsistent with known structure types from *Lemnalia* species and suggested a modified, and perhaps ring-enlarged, sesquiterpenoid structure. The alcohol group in **4** was recognized as allylic, since the alcohol methine proton at δ 4.14 was coupled ($J = 4.9$ Hz) to an olefin proton at δ 5.86. The acetoxyl methine was observed as a singlet at δ 6.81. The very low field position of this proton suggested the OAc group to be placed on the alpha C of the ketone.

Repeated hplc separation of slightly less polar column fractions yielded a diacetate, **5**, which showed highly analogous ^1H NMR features when compared with **4**. Acetylation of **4** with excess acetic anhydride in pyridine produced a diacetate which was identical with naturally occurring **5**.

Table 1. 20 MHz ^{13}C NMR Data for compounds 4 and 6–8[a]

C #	4	6	7[d]	8
1	44.2	119.8	43.8	124.8
2	138.7	25.3	140.6	131.8
3	127.1[b]	30.0	127.4	28.0[b]
4	76.2	37.4	77.3	34.2
5	190.8	38.0	190.3	40.5
6	43.8	129.6	45.3	148.3
7	28.3	138.2[b]	28.8	126.0
8	149.5[b]	27.7[c]	147.9	164.4
9	125.9	27.3[c]	121.6[b]	173.8
10	63.5	142.1[b]	123.2[b]	31.0[b]
11	35.8	75.1	130.2	29.0[b]
12	34.1	68.4	39.5	83.4
13	20.9	23.8	18.4[b]	15.0
14	18.1	15.7	18.0[b]	13.6
15	16.6	20.8	15.4	16.8
OAc	170.4	----	170.2	----
	20.5	----	20.6	----
CO_2Me	----	----	----	51.8

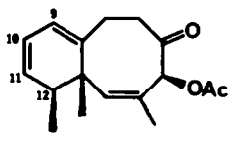
[a] assignments are based upon multiplicities and shifts determined by single-frequency off-resonance decoupling techniques unless noted otherwise. Assignments were aided by consideration of residual coupling constants.

[b,c] assignments may be reversed.

[d] off-resonance spectrum was not recorded.

In an attempt to further probe the gross structures of 4 and 5, the allylic alcohol 4 was dehydrated with *p*-toluenesulfonic acid in refluxing benzene to yield the diene 7. The diene showed $\lambda_{max} = 277$ nm ($\epsilon = 2800$), establishing the chromophore as homoannular,[9] and ^1H NMR spin-decoupling experiments suggested the diene was in a 6-membered ring. Specifically, the C-9 through C-12 constellation was delineated by decoupling olefin bands at δ 5.85 (2H, m) and δ 5.35 (1H, m), and relating these bands to a one-proton multiplet at δ 2.92. Irradiation of this latter band caused the doublet methyl at δ 1.07 to collapse to a singlet. Consideration of the number of unassigned carbon atoms and substituents led to the assignment of the remaining ring as being 8-membered. No firm data could be interpreted, however, to suggest the positions of unsaturation and oxidation.

Treatment of the hydroxyketone 4 with a saturated methanolic Na_2CO_3 solution, in air, gave an acid in moderately good yield which was immediately converted to the corresponding methyl ester with diazomethane (73% yield). Consideration of the ^{13}C (Table 1) and ^1H NMR features for this ester resulted in an assignment as structure 8, however the stereochemistry at C-12 was not unambiguously definable by spectral methods. The oxidative cleavage of 4 to yield 8 can be envisioned as proceeding first to a diacid which is converted to the delta-lactone via an internal displacement of the OH at C-10. The stereochemistry at C-12 can be predicted to be as drawn in 8, however, based upon the expected α attack required to eliminate an α-OH at C-2. This reactivity fully supports the earlier assignment of 4 as an α-OAc ketone.



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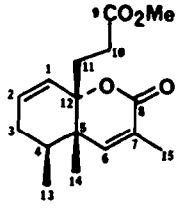

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The structures of 4 and 5 were not fully, nor unambiguously, established by the spectral data and chemical transformations mentioned above. Hence, a single crystal X-ray experiment was performed on the hydroxyketone 4. This experiment fully defined 4 as 4(S*)-acetoxy, 10(S*)-hydroxy, 5-oxo, 1(S*), 12(S*) neolemna-2(Z),8-diene (Fig. 1) and 5, therefore, as 4(S*), 10(S*)-diacetoxy-5-oxo, 1(S*), 12(S*) neolemna-2(Z), 8-diene (Fig. 1).

Reverse-phase hplc of the polar column chromatography fractions yielded the diol 6 as a colorless, viscous oil. High resolution mass spectral analysis indicated the composition $C_{15}H_{24}O_2$, which was reinforced by ^{13}C NMR data (Table 1). Intense OH absorptions at 3450 cm^{-1} in the IR spectrum of 6, coupled with ^{13}C NMR bands at 68.4 (t) and 75.1 (s), indicated two hydroxyl functionalities, one primary and the other tertiary substituted. The ^{13}C NMR spectral features also established two olefinic bonds to be present, and by consideration of the molecular formula, the diol was established to possess a bicyclic skeleton.

Treatment of the diol with 2,2-dimethoxypropane and

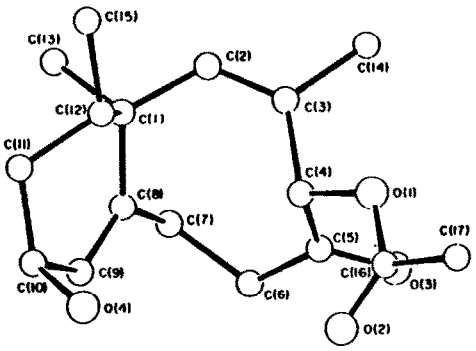
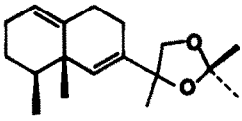


Fig. 1. A computer-generated perspective drawing of the final X-ray model for the rearranged sesquiterpenoid 4. Hydrogens are omitted for clarity and no absolute configuration is implied.

a catalytic amount of *p*-toluenesulfonic acid yielded the corresponding acetonide **9**, thus illustrating the diol to be vicinally substituted. Treatment of the diol with periodic acid in ether resulted in the expected cleavage to yield the methyl ketone **10**, which was the subject of extensive NMR analysis. Since cleavage of the vicinal diol had generated a methyl ketone, it was clear that the diol substitution in **6** had involved an isopropyl group. The methyl ketone produced was α,β-unsaturated, as evidenced by the enone absorption at 231 nm ($\epsilon = 8700$) and the unsaturated ketone IR absorption at 1665 cm^{-1}.



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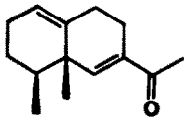

10

Extensive ^1H NMR spin-decoupling studies with the diol and with derivatives **9** and **10** allowed the structure 11,12-dihydroxyeremophilia-6,10-diene to be assigned to diol **6**. The relative stereochemistry of the ring-substituted Me groups (C-4, C-5) was established with reasonable confidence by a quantitative Eu(fod)$_3$-induced ^1H NMR shift study of the ketone **10** at 220 MHz (see experimental for details).

EXPERIMENTAL

^1H NMR spectra were recorded on a Varian HR-220 spectrometer and ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer. IR spectra were recorded on a Perkin–Elmer model 137 spectrophotometer and UV spectra were recorded on a Beckman MVI instrument. Low resolution mass spectra were obtained on a Hewlett–Packard 5930A mass spectrometer and high resolution spectra were obtained through the Department of Chemistry, University of California, Los Angeles. Optical rotations were measured on a Perkin–Elmer Model 141 polarimeter with one decimeter microcell. Melting points were determined on a Fisher–Johns melting point apparatus. All solvents were either of spectroquality or redistilled prior to use.

Collection, extraction and isolation. *Lemnalia africana* May 1898 (collection PSC-155) was collected by hand using SCUBA in shallow water (−10m) in September, 1979, in Palau, Western Caroline Islands. A $CHCl_3$/MeOH extract (41 g) was prepared by repeated extraction of the freeze-dried animal (0.9 kg), followed by removal of the solvents under vacuum. The extract was applied to a silica gel column (400 g) and rapidly eluted with a step gradient of EtOAc in isooctane.

4(S) - Acetoxy,10(S*) - hydroxy, 5-oxo, 1(S*),12(S*)neolemna - 2(Z),8 - diene* (**4**). The hydroxyketone **4** was eluted from the silica gel column with 50% EtOAc in isooctane and finally purified by reverse phase hplc (1/2" × 60 cm ODS column, 30% H_2O/MeOH). Recrystallization from benzene/isooctane (1:1) yielded 1.2 gm of **4**, m.p. 111–112° (3.0% ext.). The hydroxyketone showed $[\alpha]_D$ + 440° (*c* 1.16, $CHCl_3$) and exhibited the following spectral features: UV: λ_{max}^{MeOH} = 296 nm (ϵ = 226); IR ($CHCl_3$): 3584, 1739, 1715, 1379, 1241 and 1056 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.81 (1H, s), 5.86 (1H, d, J = 4.9 Hz) 5.51 (1H, s), 4.14 (1H, m), 2.13 (3H, s), 1.68 (3H, s), 1.01 (3H, s), 0.98 (3H, d, *J* = 6.8 Hz); MS: M^+ *m/e* = 292 for $C_{17}H_{24}O_4$ (low resolution), $M^+ - HOAc$ obs. 232.1477, calc. 232.1458, $M^+ - HOAc - H_2O$ obs. 214.1339, calc. 214.1353.

4(S),10(S*) - Diacetoxy, 4 - oxo,1(S*),12(S*)neolemna - 2(Z), 8 - diene* (**5**). The ketodiacetate **5**, an oil, was eluted from the silica column with 27% EtOAc in isooctane and subsequently purified by silica hplc (5μ silica column, 25% EtOAc in isooctane). The total yield was 61 mg (0.15% extract), and **5** showed $[\alpha]_D$ + 222° (*c* 1.10, $CHCl_3$) and the following spectral features: IR ($CHCl_3$): 3012, 1745, 1730, 1715, 1658, 1374, 1250, 1058 and 911 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.38 (1H, s), 5.87 (1H, d, *J* = 5.0 Hz), 5.51 (1H, s), 5.22 (1H, s), 2.11 (3H, s), 2.00 (3H, s), 1.70 (3H, s), 1.00 (3H, s), 0.98 (3H, d, *J* = 7.2 Hz); MS: M^+ *m/e* 334 for $C_{19}H_{26}O_5$ (low resolution).

11,12-Dihydroxyeremophilia-6,10-diene (**6**). The diol **6**, an oil, was eluted from the silica column with 40% EtOAc in isooctane and further purified by reverse phase hplc (20% H_2O in MeOH), $[\alpha]_D$ − 133° (*c* 1.32, $CHCl_3$). The diol (0.6% extract) exhibited the following spectral features: IR (film): 3450, 2994, 1460, 1362, 1045, 733 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.88 (1H, d, *J* = 2 Hz), 5.37 (1H, t, *J* ≤ 1 Hz), 3.61 (1H, d, *J* = 10 Hz), 3.42 (1H, d, *J* = 10 Hz), 1.27 (3H, s), 0.98 (3H, s), 0.96 (3H, d, *J* = 6 Hz); MS: M^+ *m/e* = 236 for $C_{15}H_{24}O_2$ (low resolution), $M^+ - H_2O$ obs. 218.1656, calc. 218.1665, $M^+ - CH_2OH$ obs. 205.1583, Calc. 205.1587.

Acetylation of hydroxyketone **4**. The hydroxyketone **4**, 16.2 mg, was treated with an excess of Ac_2O in pyridine (~2 ml each reagent) at RT for 24 hr. The mixture was diluted with H_2O and the products were extracted with Et_2O (3 × 50 ml). The combined Et_2O extracts were washed sequentially with 5% HCl (3 × 50 ml), 5% $NaHCO_3$ aq (2 × 50 ml), and next dried over $MgSO_4$ to yield **5** (16.8 mg) in 91% yield. Compound **5** produced from **4** was identical to the natural compound by IR, ^1H NMR and optical rotation analyses.

Dehydration of hydroxyketone **4** *to yield diene* **2**. A soln of **4** (25 mg) and 1 small crystal of *p*-toluenesulfonic acid in 5 ml benzene were refluxed for 30 min. The soln was cooled, diluted to 50 ml with Et_2O and washed with 5% $NaHCO_3$ (2 × 20 ml). Removal of solvents under reduced pressure yielded an oily product which was subjected to hplc purification (5 μm silica column, 20% EtOAc in isooctane) yielding **7** as a mobile oil (35.6 mg, 63%). The diene showed the following spectral features: UV: λ_{max}^{MeOH} = 277 nm (ϵ = 2780); IR (CCl_4): 3039, 1745, 1724, 1360, 1219, 1053, 1029, 887 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.58

Table 2. Quantitative Eu(fod)$_3$-induced shift data for **10**

proton (s) at C#	δ	m, J(Hz)	Δδ	R meas (Å)	θ°	R calc (Å)	%R
1 (1H)	5.43	s	0.32				
2 (2H)	2.02	m	0.16				
3 (2H)	1.55	m	0.21				
4 (1H)	1.55	m	0.99				
6 (1H)	6.82	s	1.61	6.78	7	6.62	2
8α(1H)	2.58	dd,13,6	2.00	6.03	27	5.87	3
8β(1H)	2.11	m	2.86	4.66	30	4.74	2
9 (2H)	2.25	m	0.34				
13 (3H)	2.31	s	2.72	5.22	22	5.21	0.2
14 (3H)	1.06	s	0.55	8.50	25	8.68	2.1
15 (3H)	1.03	d,6	0.43	10.10	7	10.36	2.5

(1H, s), 5.85 (2H, m), 5.56 (1H, s), 5.35 (1H, m), 2.92 (1H, q, J = 6.9 Hz), 2.11 (3H, s), 1.72 (3H, s), 1.07 (3H, d, J = 6.9 Hz), 0.97 (3H, s). MS: M^+ m/e = 274 for $C_{17}H_{22}O_3$, M^+ − HOAc m/e = 214, and M^+ − HOAc − CH_3 m/e = 199 (low resol.).

Oxidative cleavage of hydroxyketone **4** *to yield lactone* **8**. Compound **4** (20 mg) was stirred in air overnight in 10 ml of sat methanolic Na_2CO_3 soln. The soln was neutralized with 5% HCl and extracted with Et_2O (3 × 20 ml). The combined Et_2O phases were dried over $MgSO_4$ and concentrated to an oily residue under reduced pressure. The residue was mixed with an ethereal soln of CH_2N_2 and allowed to evaporate in the hood overnight. Chromatography of the residue on a silica thin-layer plate illustrated on intense UV-absorbing band which was removed and extracted to yield **8** (14 mg, 73%) as a viscous oil. The lactone showed $[\alpha]_D$ +42° (*c* 1.09, $CHCl_3$) and exhibited the following spectral features: IR (CCl_4): 3030, 1757, 1736, 1438, 1200, 1136, 1042, 1034, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.30 (1H, s), 5.94 (1H, m), 5.69 (1H, d, J = 10.3 Hz), 3.67 (3H, s), 1.93 (3H, d, J = 1.2 Hz), 0.99 (3H, s), 0.95 (3H, d, J = 6.7 Hz); MS: M^+ m/e = 278 for $C_{16}H_{22}O_4$, M^+ − OMe m/e = 247, M^+ − MeOH m/e = 246, and M^+ − $C_4H_6O_2$ m/e = 208 (low resol.).

X-Ray crystallographic structure elucidation of hydroxyketone **4**. The *Lemnalia* sesquiterpene **4** crystallized in the monoclinic space group $P2_1$ with a = 9.4078(26), b = 7.2519(24), c = 11.8948(32) Å and β = 97.832(22)° with one molecule of $C_{17}H_{24}O_4$ per asymmetric unit. Intensity data were collected on a fully automated four-circle diffractometer using graphite monochromated MoKα (0.71069 Å) radiation and a variable speed ω-scan. Of the 1574 unique reflections surveyed, 1482 (94%) were judged observed ($F_o^2 \geq 3\sigma(F_o^2)$) after correction for background, Lorentz and polarization effects. A phasing model was achieved by a direct methods approach[10] which revealed 19 of the 21 nonhydrogen atoms on an E-synthesis. The remaining nonhydrogen atoms as well as the hydrogens were located on subsequent F- and ΔF-syntheses. Full matrix least-squares refinement with anisotropic heavy atoms and fixed hydrogens have converged to a standard crystallographic residual of 0.053.[11]

Preparation of the acetonide of diol **6**. The diol **6** (19.5 mg), and a single crystal of *p*-toluenesulfonic acid were combined in 1.0 ml of 2,2-dimethoxypropane and stirred overnight at RT. The soln was partitioned between water and Et_2O, and the Et_2O layer was washed with 5% $NaHCO_3$ (2 × 25 ml) and dried over $MgSO_4$. Removal of the Et_2O under reduced pressure gave **8**, as an oil (15 mg, 65%) of sufficient purity to record the following spectral features: IR ($CHCl_3$): 2976, 1451, 1370, 1242, 1058, 973, 853 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.83 (1H, s), 5.39 (1H, t, J ≃ 1 Hz), 3.99 (1H, d, J = 10 Hz), 3.73 (1H, d, J = 10 Hz), 1.45 (3H, s), 1.41 (3H, s), 1.38 (3H, s), 0.97 (3H, s), 0.94 (3H, d, J = 6 Hz); MS: M^+ m/e 276 for $C_{18}H_{28}O_2$ (low resol.).

Periodic acid cleavage of diol **6** *to yield ketone* **10**. The diol **6** (12.5 mg) in 10 ml Et_2O was treated with an excess of H_5IO_6 in Et_2O. After 30 min the soln was partitioned between Et_2O and H_2O and the Et_2O layer (50 ml) and dried over $MgSO_4$. Removal of solvent at reduced pressure yielded **10** (9 mg, 82%) as an oil of sufficient purity for extensive spectral analysis. Ketone **10** showed the following features: UV: λ_{max}^{MeOH} = 231 nm (ε = 8700); IR ($CHCl_3$): 3012, 1665, 1637, 1264, 1232, 1066, 995, 966, 908 cm^{-1}; MS: M^+ m/e = 204 for $C_{14}H_{20}O$ (low resol.). (^{1}H NMR data are listed below.)

Quantitative Eu(fod)$_3$*-induced shift* ^{1}H *NMR study of ketone* **10**. Aliquots of Eu(fod)$_3$ in $CDCl_3$ (19 mg/100 μl) were added to **10** and ^{1}H NMR spectra were recorded at 220 MHz. When a total of 100 μl of the shift reagent soln had been added, the spectrum obtained showed the resolution of the majority of the protons in **10**. The methylene protons at C-8 and C-9 were observed as 2H multiplets, however, at this concentration. By spin-decoupling, assignments of the isolated $-CH_2-CH_2-$ group (C-8–C-9) and the $\diagdown$=CH–CH_2–CH_2–CH(CH_3)$\diagup$ constellation (C-1–C-4) were confidently made, and these assignments are tabulated below. Chemical shifts (δ) were measured both by direct measurement with the non-shifted spectrum and by extrapolation, using Δδ, to zero concentration. Protons at C-6 and C-8, as well as methyls C-13, C-14 and C-15, were quantitatively evaluated using molecular models and the simplified form of the general dipolar (pseudocontact) contribution equation[12] (see Table 2).

Acknowledgements—We (RRI and WF) wish to gratefully acknowledge financial support for this research from the National Science Foundation under grant OCE 78-03924. Collections and field studies of the Palauan soft-coral fauna were supported through our use of the research vessel ALPHA HELIX, also supported by a grant from the National Science Foundation. JC acknowledges research support provided by NIH-CA-24487.

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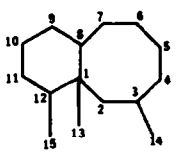
[4]B. F. Bowden, J. C. Coll and S. J. Mitchell, *Aust. J. Chem.* **33**, 1833 (1980).
[5]Based upon the biogenetic relationship of **4** and **5** with the nardosinane (lemnalane)[6] sesquiterpenoids which are major components of *Lemnalia* species,[7] we suggest the semisystemic name neolemnane and the numbering sequence below for this new ring system.



neolemnane

[6]B. F. Bowden, J. C. Coll and S. J. Mitchell, *Aust. J. Chem.* 33, 885 (1980).

[7]B. Tursch, J. C. Braekman, D. Daloze and M. Kaisin In *Marine Natural Products, Chemical and Biological Perspectives*, (Edited by P. J. Scheuer) Vol. II, Chap. 4. Academic Press, New York (1978).

[8]We wish to thank Dr. J. Verseveldt, for identification of this soft-coral.

[9]A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*. Pergamon Press, New York (1974).

[10]All crystallographic calculations were done on a PRIME 400 computer operated by the Materials Science Center and the Department of Chemistry, Cornell University. The principal programs used were REDUCE and UNIQUE, data reduction programs, M. E. Leonowicz, Cornell University, 1978; BLS78A, anisotropic block-diagonal least-squares refinement, K. Hirotsu and E. Arnold, Cornell University, 1980; XRAY76, the X-ray system of crystallographic programs, edited by J. M. Stewart, University of Maryland, *Tech. Rep.* TR-445, March 1976; ORTEP crystallographic illustration program, C. K. Johnson, Oak Ridge, ORNL-3794; NULTAN-78 (locally modified) A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. University of York, England. Principal author P. Main. For literature description of MULTAN see: G. Germain, P. Main and M. M. Woolfson, *Acta Cryst. Sect. B.* 26, 274–285 (1970), and M. M. Woolfson, *Ibid. A* 33, 219–225 (1977).

[11]Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

[12]R. E. Sievers (Ed.) *Nuclear Magnetic Resonance Shift Reagents*. Academic Press, New York (1973).