

SPECIALIA

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$\Delta^{9(15)}$ -Africanene, a new sesquiterpene hydrocarbon from the soft coral *Sinularia erecta*

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Summary. The isolation and structural elucidation of $\Delta^{9(15)}$ -africanene from the soft coral *Sinularia erecta* is presented.

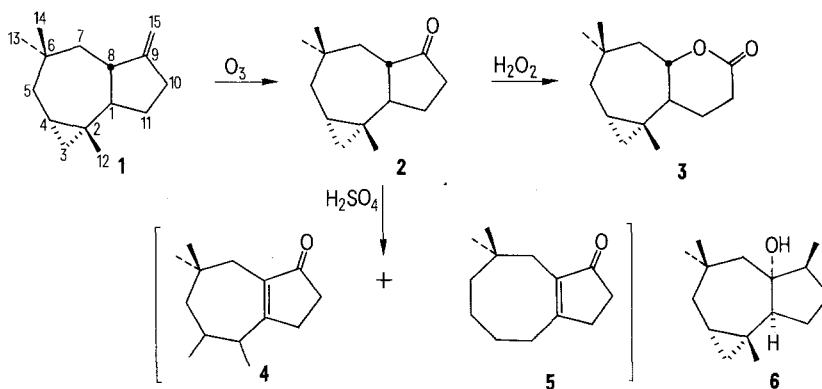
The isolation of a number of interesting natural products from soft corals of the genus *Sinularia* prompted us to examine these corals from the Gulf of Eilat (Red Sea)¹⁻⁹. We now wish to report the isolation of a new sesquiterpene from one of these corals, *Sinularia erecta*.

S. erecta was unusual in that it contained a high percentage of hydrocarbons (1.5%, dry weight) and over 95% of its oil consisted of a single compound, (**1**). Compound **1**, $C_{15}H_{24}$, which we name $\Delta^{9(15)}$ -africanene, could be purified by $AgNO_3$ -silica gel chromatography followed by preparative VPC (SE-30, 5% on GCQ, 120 °C). Its spectral properties were $[a]_D^{24} + 86$ (c 3.7 in $CHCl_3$); MS (70 eV): 204 (M^+ , 77%), 135 (100%); 1H -NMR (60 MHz, CCl_4): 0.16 m (1 H), 0.52 m (2 H), 0.89 s (3 H), 0.97 s (3 H), 1.04 s (3 H), 4.60 brs (1 H) and 4.80 brs (1 H); IR (neat) 3080, 3060, 1650, 1380, 1365, 1020, 885 and 875 cm^{-1} ; UV end absorption only; ^{13}C -NMR (22.63 MHz, $CDCl_3$, ppm from TMS, tentative

assignments): 157.8 s (C-9), 104.5 t (C-15), 52.3 d (C-1), 50.9 t (C-7), 42.8 t (C-5), 41.8 d (C-8), 34.0 q (C-14), 33.0 s (C-6), 33.0 t (C-10), 27.4 t (C-11), 24.1 q and 20.5 q (C-12 and C-13), 22.9 t (C-3), 22.0 d (C-4) and 18.5 s (C-2).

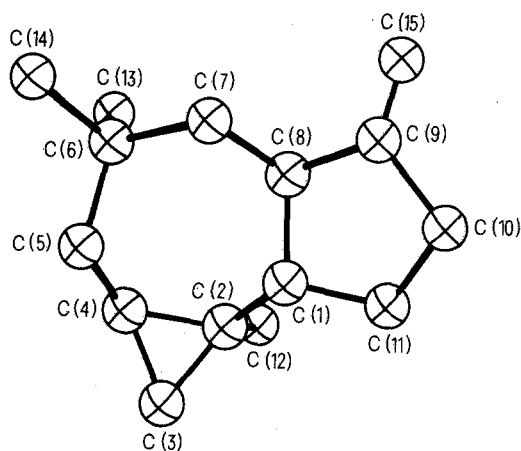
The 1H -NMR signals at 0.16 and 0.52 together with the ^{13}C -NMR signals at 18.5, 22.0 and 22.9 are indicative of a trisubstituted cyclopropane. An exocyclic methylene is indicated by ^{13}C -NMR signals at 157.8 and 104.5 and the two protons resonating at 4.60 and 4.80 in the 1H -NMR. Since compound **1** has 4 formal unsaturations the structure must contain 2 additional carbocyclic rings. The following reactions were carried out to elucidate the structure.

Ozonolysis of **1** followed by reductive work-up (either with Zn in 1% CH_3CO_2H -THF (1:1) or, to avoid isomerization *a* to the carbonyl, with Ph_3P) gave ketone **2**: $C_{14}H_{22}O$, m.p. 63 °C (benzene); $[a]_D^{24} + 182$ (c 3.5, in $CHCl_3$); IR (KBr)



3050, 1740, 1365, 1385, 1020 cm^{-1} ; UV (CH_3CN) 305 nm ($\epsilon=25$); MS (70 eV): 206 (25%) and 139 (100%)¹⁰. The 1740 cm^{-1} absorption in the IR spectrum suggests that a cyclopentanone is part of **2**. The Bayer-Villiger reaction using H_2O_2 in acetic acid or *m*-chloroperoxy-benzoic acid in CH_2Cl_2 in the presence of sodium metaphosphate gave the expected lactone **3** (scheme): $\text{C}_{14}\text{H}_{22}\text{O}_2$, m.p. 31 °C, $[\alpha]_D^{24} + 24$ (c 3.5 in CHCl_3), MS (70 eV) 222 (M^+ , 20%); IR (neat) 3060, 1740, 1215, 1020 cm^{-1} . $^1\text{H-NMR}$ (270 MHz, CDCl_3): 0.24 brs (H-3 β), 0.61 m (H-4 and H-3 α), 0.95 s, 1.04 s and 1.06 s (3 H each, Me's 12, 13 and 14), 1.34 m (H-1 and H-7 α), 1.98 ddd ($J=13.2, 3.5$ and 2.3 Hz, H-7 β), 2.3 ddd ($J=16.7, 9$ and 6 Hz, H-10), 2.56 ddd ($J=16.7, 6$ and 4.8 Hz, H-10') and 4.48 ddd ($J=11.5, 10.5$ and 3.5 Hz, H-8). Most significant in the $^1\text{H-NMR}$ spectrum is the signal at δ 4.48 ppm, attributed to the proton geminal to the etheric lactone oxygen, which looks like a double triplet. Its neighbours were confirmed by a double irradiation experiment $J_{\text{H-7}\alpha, \text{H-8}}=11.5$, $J_{\text{H-1}, \text{H-8}}=10.5$, and $J_{\text{H-7}\beta, \text{H-8}}=3.5$ Hz. The 11.5 and 10.5 couplings may be reversed. This signal requires that the etheric oxygen and hence also the methylene of **1** have to be next to the ring junction. The most likely structure which can be suggested, based on the above data and biogenetic considerations (the isoprenoid rule), is 2,6,6-trimethyl-9-methylenebicyclo[6.3.0.0^{2,4}] undecane¹¹; a skeleton which has already been found in a marine metabolite (**6**) vide infra. Further support for the relative location of the carbonyl and the cyclopropane ring was obtained by acidic treatment of compound **2** (20 min in cold 95% H_2SO_4), which gave a mixture of mainly 2 α, β -unsaturated ketones, most likely of structures **4** and **5** or their possible stereoisomers (UV: 240 nm ($\epsilon=8000$), IR: 1695 and 1635 cm^{-1} , $^1\text{H-NMR}$: no cyclopropane; several singlet and doublet methyls (comparison of the 90 and 270 MHz spectra) and 7 allylic and α -to carbonyl protons at δ 2.0–2.5 ppm) (scheme). The 270 MHz $^1\text{H-NMR}$ spectra assignments of compound **2** and **3** (assisted in the case of compound **2** also by an LIS study; $\Delta\delta$ H-8, 10 α , 10 β > H-7 β > H-7 α > H-5 α , 1 > H-3 β > H-3 α , 4, Me-12, 13, 14) are in good agreement with the suggested tricyclic structure. However, no unequivocal stereochemistry could be deduced.

Searching the literature for a similar carbocyclic skeleton brought us to africanol (**6**) which has been isolated from *Lemnalia africana*¹². Compound **6** is reported to undergo acidic elimination to give among other isomers the Δ^8 isomer, which could have been a possible isomerization product of **1**. Attempts conducted in this direction gave,



A computer generated perspective view of the relative stereostructure of **1**.

after prolonged heating of **1** in acetic acid, a mixture of the starting material and its $\Delta^{9(10)}$ isomer only – preventing a comparison between **1** and **6**. Being unable to determine the stereochemistry of **1**, we turned to an X-ray analysis.

Crystals of ozonolysis product **2** belonged to the orthorhombic space group $P2_12_1$. Since the crystals diffracted poorly, the analysis was done in a nitrogen cold stream ($\sim -100^\circ\text{C}$). Cell constants were $a=6.429$ (4), $b=25.962(8)$ and $c=30.126(8)$ Å and a calculated density ($z=16$) of 1.10 g/cm^3 . This requires 4 molecules of $\text{C}_{15}\text{H}_{24}$ in the asymmetric unit. All unique data with $2\theta \leq 114^\circ$ were measured on a Syntex $P2_1$ diffractometer using graphite monochromated $\text{CuK}\alpha$ (1.54178 Å) X-rays and $1^\circ \omega$ -scans. After correction for Lorentz, polarization and background effects, 1763 of the 3853 (46%) reflections were judged observed ($F_o^2 \geq 3 \sigma(F_o^2)$). The 350 largest E 's were phased using a multisolution weighted tangent formula approach¹³. This revealed 50 plausible nonhydrogen atoms in an E-synthesis and the remaining 10 were found in an F-synthesis. Anisotropic refinement of the nonhydrogen atoms has converged to $R=0.119$ and no attempt has been made to find hydrogens.

1 of the 4 molecules of the asymmetric unit is shown in the figure. The X-ray experiment defined only the relative configuration. 1 of the 2 enantiomers is given in the figure below. The X-ray data revealed a trans junction between the 5- and 7-membered rings; the 5-membered ring being in the envelope conformation with C(1) serving as the flap. The absolute configuration of **1** was deduced from the CD spectrum of compound **2** and is as shown in the drawing of **1** in the scheme. The value of $\Delta\epsilon + 2.61$ ($\lambda_{\text{max}}=299\text{ nm}$ in MeOH) is in the same order as the corresponding trans hydrindanone¹⁴; the main contribution to the Cotton effect coming from the distorted cyclopentanone ring while the rest of the skeleton (in both possible conformations) with the methyl group essentially compensates itself.

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- 9 J.C. Coll, S.J. Mitchell and G.J. Stokic, *Tetrahedron Lett.* 1977, 1539.
- 10 $^1\text{H-NMR}$ (270 MHz, CDCl_3): δ 0.28 dd ($J=4.1$; 4.4 Hz, H-3 β), 0.55 dddd ($J=4.4$; 8.2; 6.0; 6.5 Hz, H-4), 0.64 dd ($J=4.1$; 8.2 Hz, H-3 α), ~ 0.91 s (CH_3 -14), 1.01 s (CH_3 -12 and 13), 0.9 ddd ($J=2.2$; 15; 6 Hz, H-5 α), 1.07 dd ($J=13.6$; 11 Hz, H-7 α), 1.56 ddd ($J=11.5$; 11.5; 6.5 Hz, H-1), ~ 2.5 ddd ($J=13.6$; 3.7; 2.2 Hz, H-7 β) and 2.4 m (H-8, 10 α and 10 β). $^{13}\text{C-NMR}$ (22.63 MHz CDCl_3 , tentative assignments): 221 s (C-9), 49.8 d and 48.1 d (C-1 and 8), 45.8 t (C-7), 43.4 t (C-5), 38.9 t (C-10), 33.4 q (C-14), 33.2 s (C-6), 23.5 t (C-11), 23.5 q and 20.5 q (C-12 and 13), 22.0 t (C-3), 23.5 d (C-4), and 18.8 s (C-2).
- 11 The same compound has been isolated by Brackman et al., from *Sinularia polydactyla*. *Experientia* 36, 893 (1980).
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