Chemical studies of marine invertebrates. XXXVIII[1]. $\Delta^{9(15)}$-Africanene, a new sesquiterpene hydrocarbon from *Sinularia polydactyla* (Coelenterata, Octocorallia, Alcyonaceae)[2]

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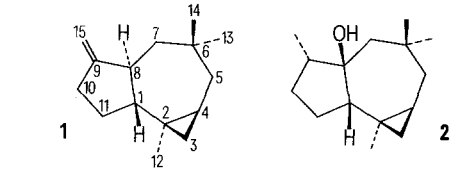
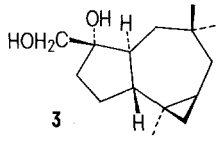
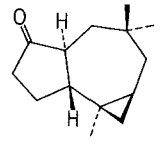
Summary. The isolation and structure determination of $\Delta^{9(15)}$-africanene (**1**) from the soft coral *Sinularia polydactyla* is described.

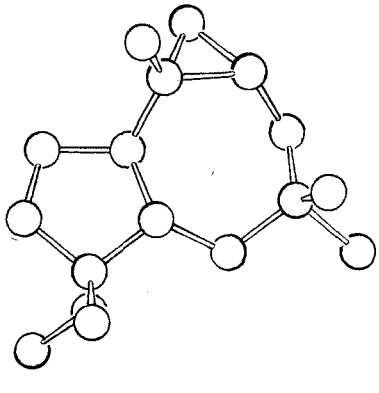
Several recent reports[4-8] have shown that soft corals of the genus *Sinularia* constitute an interesting source of terpenoids. We have now investigated a further member of this genus: *Sinularia polydactyla,* collected at Laing Island (Papua-New Guinea). Its major compound is a sesquiterpene hydrocarbon (**1**) whose structure determination is discussed here.

Finely ground specimens of *S. polydactyla* (200 g) were extracted with CH_2Cl_2 at room temperature, affording 6.5 g of an oily material which was chromatographed twice on a silica gel column (eluent: hexane) to yield 180 mg of hydrocarbon **1** (95% pure by GC, OV-1, 110 °C). **1**: $[\alpha]_D$ +95° (c=0.4, $CHCl_3$); MS: M^+ 204 (17) $C_{15}H_{24}$, 189 (19), 175 (13), 162 (43), 161 (35), 148 (18), 147 (26), 133 (77), 121 (35), 119 (45) ... 41 (100); IR (neat): 3080, 2950, 1660, 1460, 1385, 1365, 1140, 885, 875 cm^{-1} (exomethylene); ^{1}H-NMR (60 MHz, δ, $CDCl_3$): 0.2 to 0.56 (c m, 3 H, cyclopropane C–H), 0.88, 0.95, 1.03 (s, 3 H each, tertiary methyls), 4.70 and 4.87 (broad singlets, $C=CH_2$). These spectral data are consistent with a tricyclic sesquiterpene which contains 3 tertiary methyls, an exocyclic methylene and a cyclopropane ring bearing 3 hydrogens. This suggests a close relationship between **1** and africanol (**2**), a sesquiterpene alcohol isolated previously[9,10] from another soft coral, *Lemnalia africana.* Since a direct correlation between both compounds did not seem straightforward, in view of the small amount of **1**, an X-ray diffraction analysis was performed on diol **3**, obtained by OsO_4 oxidation of **1**.









Computer drawing of **3**.

Diol **3**: m.p. 112–114 °C (from hexane), M^+ 238 (3.5) $C_{15}H_{26}O_2$, 220 (8), 207 (100), 190 (26), 186 (10), 138 (26), 133 (23), 123 (25), 109 (47), 107 (40); ^{1}H-NMR (60 MHz, δ, $CDCl_3$): 0.2 to 0.67 (3 H, multiplet, cyclopropane CH), 0.9, 1.0, 1.05 (s, 3 H each, tertiary CH_3), 3.53 (AB, $-CH_2OH$); IR (KBr): ν_{OH} 3400 cm^{-1}. **3** crystallized in space group C 2, with a=32.261, b=6.106, c=16.105 Å, β=115.80; Z=8. 2005 independent reflections were measured on a Picker diffractometer (CuKα radiation) with 1095 being observed at 2 Θ max=120°. The structure was solved using the Multan 78 programs[11] and the refinements were realised using the X-ray 72 programs[12]. R_{final}=0.157.

A computer drawing showing the relative configuration of **3** is depicted in the figure. It follows that the hydrocarbon of *S. polydactyla* has structure **1**. Application of the octant rule to ketone **4** [CD (c=0.5; CH_3OH; 22°): $[\Theta]_{250}$ 0; $[\Theta]_{298}$ +8.769; $[\Theta]_{330}$ 0; m.p. 62–4 °C; $[\alpha]_D$ +176° (c=0.91, $CHCl_3$); M^+ 206; $C_{15}H_{22}O$], obtained by Na IO_4 cleavage of diol **3**, shows that its absolute configuration is the same as that of africanol[10]. Consequently, **1** is $\Delta^{9(15)}$-africanene. The same compound has been independently isolated by Kashman et al.[3] from a Red Sea sample of *Sinularia erecta.* The identity of both compounds was demonstrated by a comparison of the ketone **4** with the corresponding ketone deriving from the *S. erecta* compound (m.p., [α], IR, NMR, MS and GC on SP-1000 and Carbowax 20 M columns).

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