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THE ISOLATION OF TWO SIMPLE γ-LACTONIC CEMBRANOLIDES FROM THE SOFT CORAL *SINULARIA MAYI*

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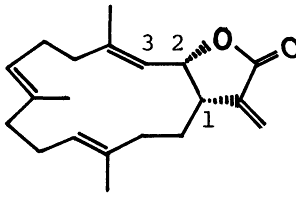
Two simple γ-lactonic cembranolides were isolated from the soft coral *Sinularia mayi* Lüttschw. and structurally elucidated on the basis of spectral and chemical evidence.

We recently described the structures of two new cembrane diterpenoids cembrenene and mayol from the soft coral *Sinularia mayi* Lüttschw.[1] Further investigation of the same species has resulted in the isolation of two isomeric cembranolides (**1**) and (**2**), and we now wish to report the structures of these compounds. While the isolation of compound (**1**) was independently reported by Coll et al. from the Australian soft coral *Lobophytum michaelae*,[2a] the relative stereochemistry[2b] of the lactone ring of **1** has not yet been established. Compounds (**1**) and (**2**) were isolated from the dichloromethane soluble material of the methanol extract of dried animal in 0.02 and 0.001% yields, respectively, by a combination of column and preparative TLC.

Compound (**1**)[3] was identified by the coincidence of the IR and ^{1}H NMR spectra as those of the authentic sample.[2a] The assignment of a *cis*-fusion of the lactone ring of **1** was based on the following results. The lactonic methine proton (H-2) appeared at δ 5.39 as a doublet of doublets ($J_{1,2}$=7.5, $J_{2,3}$=10.0 Hz) whose J values were fully compatible with those of lobohedleolide carring a *cis*-fused γ-lactone ring,[4] and the NOE (5%) was observed between H-1 (δ 3.01) and H-2 protons in **1**. Reduction of **1** with $(i\text{-Bu})_2$AlH in toluene (-78 °C), after quenched with MeOH, followed by treatment with $NaBH_4$, afforded an alcohol (**3**), $C_{20}H_{32}O_2$ ($M^{+\cdot}$ 304); mp 105.0-106.0 °C; $[\alpha]_D$ +82.9° (c 1.11, $CHCl_3$); IR($CHCl_3$) 3620, 3350, 1665, 1630, 885 cm^{-1}. In the ^{1}H NMR spectrum[5] of **3**, the secondary alcohol methine proton (H-2) gave rise to a doublet of doublets ($J_{1,2}$=1.5, $J_{2,3}$=8.5 Hz) at δ 4.72, the coupling mode of which is nearly identical with that of mukulol ($J_{1,2}$=1.0, $J_{2,3}$=9.0 Hz),[6] indicating the *cis* stereochemistry of C-2 hydroxyl and isopropenyl groups in **3**.

Compound (**2**), an oil, $[\alpha]_D$ -29.0° (c 3.40, $CHCl_3$), was shown to possess the same molecular formula $C_{20}H_{28}O_2$ as **1** by high mass measurement ($M^{+\cdot}$ 300.2109) and therefore was an isomer of **1**. The ^{13}C NMR spectrum of **2** listed below contained twenty signals for all the functional moieties as **1**,[3] suggesting that **2** would be also a cembranolide: δ 15.3q, 15.6q, 16.4q, 24.0t, 24.0t, 32.1t, 36.0t, 38.4t, 38.9d, 43.1d, 79.1d, 121.3t, 123.6d, 125.3d, 125.9d, 131.4s, 133.6s, 140.9s, 141.2s, 170.4s. The IR and ^{1}H NMR spectra indicated the presence of an α-methylene-γ-lactone (IR 1755, 1655



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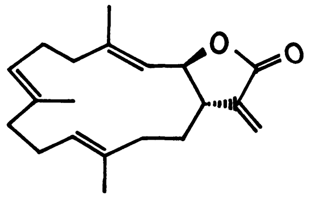

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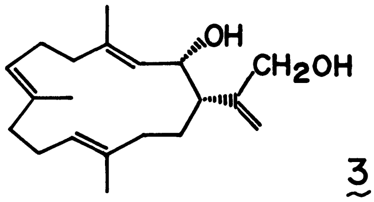

3

cm^{-1}: δ 5.57, 1H, d, J=2.2 Hz; 6.22, 1H, d, J=2.5 Hz), three methyl-bearing trisubstituted double bonds (δ 1.61, 6H, br s; 1.72, 3H, d, J=1.0 Hz; 4.80-5.10, 2H, overlapping m; 5.08, 1H, br d, J=10.0 Hz), an allylic methine proton (δ 2.64, 1H, m) and a lactonic methine proton (δ 4.86, 1H, dd, J=10.0, 3.5 Hz). Irradiation of the proton at δ 2.64 collapsed the doublets at δ 5.57 and 6.27 to sharp singlets and the lactonic methine proton at δ 4.86 to a doublet (J=10.0 Hz). These finding clearly showed that the lactonic methine proton at δ 4.86 coupled to the vinyl proton at δ 5.08 (br d, J=10.0 Hz), confirming the allylic nature and ring size of the lactone. The above ^{1}H NMR spectral features of **2** closely resembled to those of **1**[3] except for the large difference of the lactonic methine proton which appeared as a doublet of doublets at δ 4.86 (J=10.0, 3.5 Hz)[7] in **2** and δ 5.39 (J=10.0, 7.5 Hz) in **1**. Microozonolysis[8] of **2** followed by GC-MS analysis yielded two equivalents of 4-oxopentanal by comparison with that obtained from geraniol,[2a] hence confirming the cembrane skeleton of **2**. The E-geometry of the trisubstituted double bonds was deduced from the ^{13}C chemical shifts of the vinylic methyls (δ 15.3, 15.6, 16.4)[9] as in the case of **1**. Thus, compound (**2**) was assigned a *trans*-fused isomer of the γ-lactonic ring of **1**.

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3. $C_{20}H_{28}O_2$ ($M^{+\cdot}$ 300); mp 98.0-99.0 °C; $[\alpha]_D$ +89.9° (c 1.90, $\mathrm{CHCl_3}$); IR($\mathrm{CHCl_3}$) 1765, 1665 cm^{-1}; ^{1}H NMR($\mathrm{CDCl_3}$) δ 1.56 (6H, br s), 1.66 (3H, d, J=1.0 Hz), 3.01 (1H, m), 4.80 (2H, br t, J=8.0 Hz), 4.99 (1H, br d, J=10.0 Hz), 5.39 (1H, dd, J=10.0, 7.5 Hz), 5.50 (1H, d, J=2.5 Hz), 6.22 (1H, d, J=3.0 Hz); ^{13}C NMR($\mathrm{CDCl_3}$) δ 15.2q, 15.2q, 15.8q, 23.5t, 24.6t, 27.3t, 36.4t, 39.8t, 40.0t, 43.5d, 78.2d, 120.3d, 120.3t, 124.0d, 125.6d, 133.7s, 133.7s, 139.2s, 142.4s, 170.7s. Lit.,[2a] mp 101-102 °C, $[\alpha]_D$ +77.9° (c 0.21, $\mathrm{CHCl_3}$).
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5. ^{1}H NMR($\mathrm{CDCl_3}$) δ 1.58 (6H, s), 1.60 (3H, d, J=1.0 Hz), 3.99 (1H, d, J=12.5 Hz), 4.18 (1H, d, J=12.5 Hz), 4.72 (1H, dd, J=8.5, 1.5 Hz), 4.93 (1H, br s), 5.07 (2H, m), 5.14 (1H, br s), 5.44 (1H, br d, J=8.5 Hz).
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