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A NOVEL TETRACYCLIC POLYKETAL FROM THE MARINE RED ALGA LAURENCIA CHILENSIS

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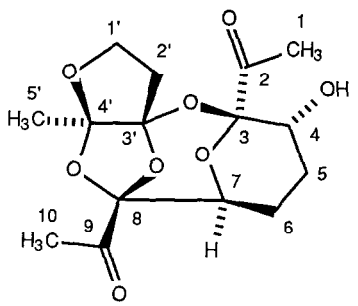
SUMMARY. An unusual tetracyclic polyketal has been isolated from the red alga Laurencia chilensis. The structure was established by x-ray diffraction and spectral methods.

Laurencia chilensis has been examined for novel secondary metabolites, and reports on aromatic[1], sesquiterpenoid[2,3], and 2-methyl-3(H)-furanone[4] derived compounds have appeared. We now wish to report the isolation and characterization of the novel tetracyclic polyketal shown as **1**.



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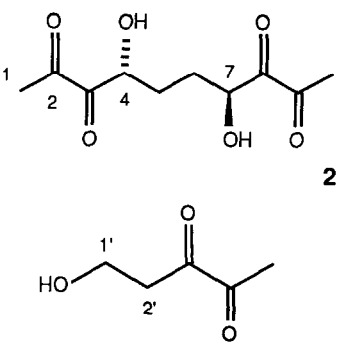

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Laurencia chilensis was collected in February, 1980 at Cocholgüe, Bahia de Concepcion, Chile. The chloroform soluble extract was chromatographed on silica gel and compound **1** recrystallized from ethyl acetate, m.p. 182-185° C. Preliminary spectral data did not suggest any previously described structures and **1** was characterized by x-ray diffraction.

Compound **1** crystallized in the centrosymmetric monoclinic space group $P2_1/c$ with **a**=16.224(3), **b**=6.157(2), **c**=15.757(3) Å, and **β**=108.93(1)° with one molecule of composition $C_{15}H_{20}O_8$ in the asymmetric unit. All unique diffraction maxima with $2\theta < 114°$ were collected using a graphite monochromated Cu Kᾱ

radiation (1.54178 Å) and variable speed, 1° ω-scans. After correcting for Lorentz, polarization, and background effects, 1895 (81%) of the 2330 reflections were judged observed ($F_o > 3\sigma(F_o)$). A phasing model was easily found, and block diagonal least-squares refinements with anisotropic heavy atoms and isotropic hydrogens have converged to a standard crystallographic residual of 0.066.[5,6]

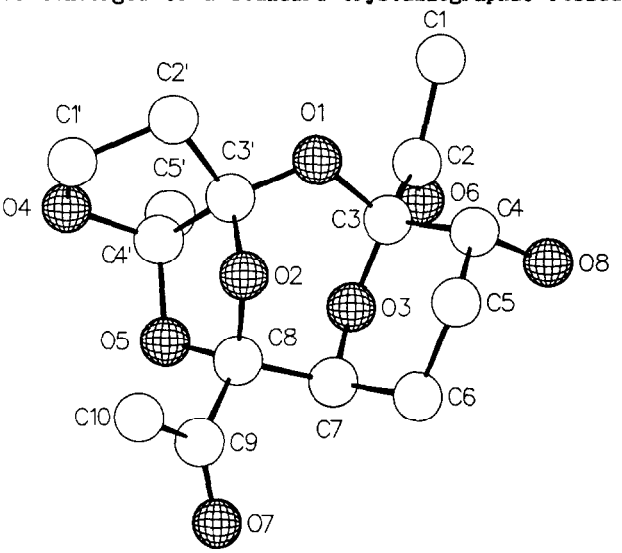

Figure 1. A computer generated perspective drawing of the final x-ray model of compound **1**. Hydrogens are omitted for clarity, and the naturally occurring substance is a racemate.

The spectral data are in complete agreement with structure **1**. The MS shows a parent ion at m/z of 328 and major fragment ions at 142, 100, 99, 55, and 43 (base peak). The IR has bands at 3480, 1780, 1720 (br), 1640, 1570, 1250, 1045, and 730 cm^{-1}. The ^1H NMR ($CDCl_3$, 360MHz) has resonances at δ 4.55 (d, H7), 4.07 (app. q, H1'), 3.97 (m, H1'), 3.96 (dd, H4), 2.57 (m, H5), 2.39 (m, H2'), 2.36 and 2.34 (s, 3H each, H1 and H10), 2.19 (m, H6), 1.62 (m, H5), 1.56 (s, 3H, H5'), 1.52 (m, H6), and 1.26 (app. t, H2'). Although **1** has six chiral centers, it is a naturally occurring racemate. Compound **1** can be dissected into meso diol **2** and achiral **3** by breaking all of the ketal bonds.

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5. For a description of the crystallographic programs see Sun, F.; Liang, X.T.; Yu, D.; Xu, C.F.; Clardy, J. Tetrahedron Lett. **1986**, 27, 275-278.

6. Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K. Please give a complete literature citation when ordering.

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