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STRUCTURE OF GÜIMAREDIOL, A NEW REARRANGED SESQUITERPENOID FROM THE RED ALGA LAURENCIA SP.

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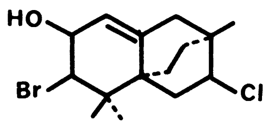
The structure of güimarediol, a new brominated tricyclic sesquiterpene with a new rearranged isoprenoid skeleton isolated from the red seaweed Laurencia sp., was determined by spectroscopic methods and X-ray crystallography.

In a previous communication1) we have reported the isolation of two novel sesquiterpenoids, rhodolaureol (1) and rhodolauradiol (2), from the red seaweed Laurencia sp. (Rhodomelaceae), collected off Güimar, Tenerife, Canary Islands. We describe herein the structure of an additional sesquiterpene, güimarediol (3), isolated from the same alga (26 mg, 0.08% of lipid weight).

Compound 3 was isolated on previous acetylation (Ac_2O/Py/25 °C) of the non-resolved and more polar chromatographic fractions; $C_{17}H_{25}BrO_3$, M^+ at m/z 356, 358; mp 94-95 °C, $|\alpha|_D^{27}$ +30° (c 1.2, $CHCl_3$). IR (KBr) 3550, 3060, 1710, 1640, 1105, 970, 880, 800, and 710 cm^{-1}. ^1H-NMR spectrum ($CDCl_3$) showed absorptions for two quaternary methyl groups at δ 1.09 and 1.39 (s, 3H each), one acetate-methyl at 2.09 (s, 3H), one proton α to a bromine at 4.23 (1H, d, J= 4.5 Hz), two exocyclic methylene protons at 4.58 (bs, 1H each), and one proton α to an acetate at 5.45 (dt, J= 4.5 and 4 Hz).



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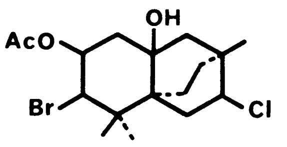

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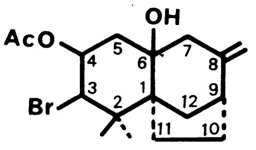

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A single crystal of the monoacetate 3 was subjected to X-ray analysis to determine its structure. The compound crystallized in the monoclinic crystal system with a = 18.799(2), b = 6.086(3), c = 15.144(9) Å, β = 109.54(5)°. Systematic absences, chirality and a rough density measurement were accommodated by space group C2 with one molecule of composition $C_{17}H_{25}BrO_3$ forming the asymmetric unit. All unique diffraction maxima with $2\theta \leq 114°$ were collected using graphite monochromated CuKα radiation and 1° ω-scans. Of the 1282 reflections measured, 823 (64%) were recognized for observed reflections after correction for Lorentz, polarization and background effects. The Patterson synthesis was used to locate the Br position and the resulting Br-phased electron density synthesis, which was complicated by a pseudomirror plane, was interpreted to give most of the non-hydrogen position.[2] Successive electron density syntheses and difference syntheses revealed the remaining non-hydrogen atoms and hydrogens. Full-matrix least-squares refinements with fixed isotropic hydrogens, anisotropic non-hydrogens and anomalous scattering corrections for bromine have currently converged to a standard crystallographic residual of 0.084 for the structure shown in Fig. 1.[3] The enantiomer refined to 0.088.

We propose to designate this new rearranged sesquiterpene ring system as güimarane (2,2,8-trimethyl-tricyclo $|7,2,1,0^{1,6}|$ dodecane), after the place where the seaweed was collected.

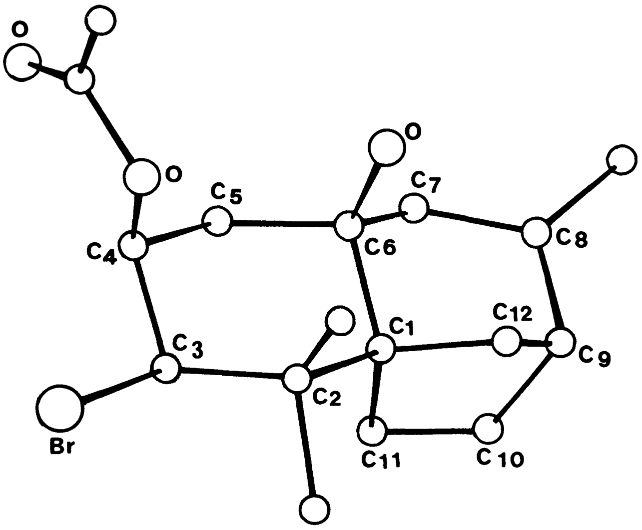

Fig. 1. A computer generated perspective drawing of güimarediol monoacetate. Hydrogens are omitted for clarity and the absolute configuration was decided by anomalous scattering measurements.

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References

1) A.G. González, J.D. Martín, V.S. Martín, M. Norte, and R. Pérez, Tetrahedron Lett., 23, 2395 (1982).
2) The programs used are described in E. Arnold and J. Clardy, J. Am. Chem. Soc., 103, 1243 (1981).
3) Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre.

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