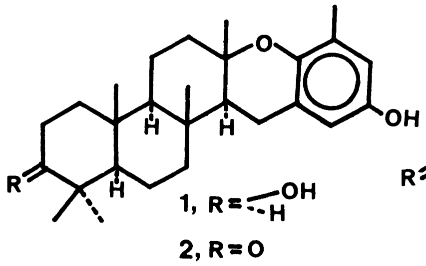
CHEMISTRY LETTERS, pp. 1649 - 1652, 1984.

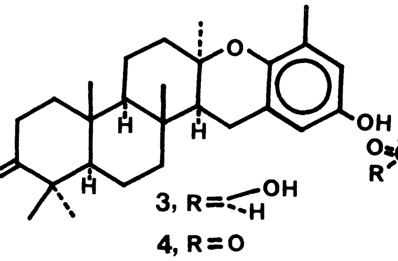
ISOLATION AND X-RAY STRUCTURAL DETERMINATION OF THREE NEW DITERPENOIDS FROM THE MARINE ALGA *TAONIA ATOMARIA*$^{1)}$

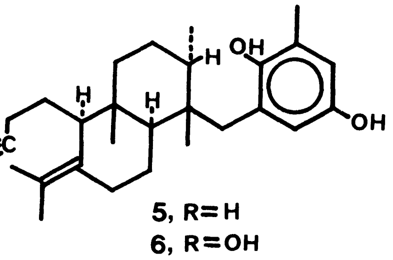
Antonio G. GONZALEZ, Julio D. MARTIN,* Cirilo PEREZ, Juana ROVIROSA,
Bruce TAGLE,† and Jon CLARDY†*
Instituto de Química Orgánica, Universidad de La Laguna, and Instituto
de Productos Naturales Orgánicos del C.S.I.C., Tenerife, Spain
† Department of Chemistry-Baker Laboratory, Cornell University, Ithaca,
NY 14853, U.S.A.

Two new peroxylactones and one hemilactal triacetate based on the atomaric acid skeleton were isolated from the brown seaweed *Taonia atomaria*. These unusual structures have been elucidated on the basis of X-ray crystallography.

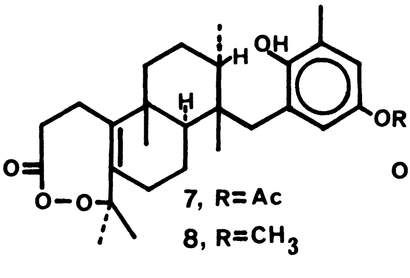
In our studies on nonenzymic interconversions between the compounds taondiol (1)$^{2)}$ and atomaric acid (6),$^{3)}$ co-existing metabolites in the seaweed *Taonia atomaria*, we have concluded that the overall rearrangement process could not proceed in a concerted manner but would involve a series of intermediates among which the non-isolated aldehyde 5 was included.$^{4)}$

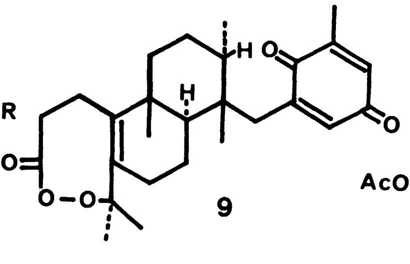

1, R=$<^{\text{OH}}_{\text{H}}$
2, R=O

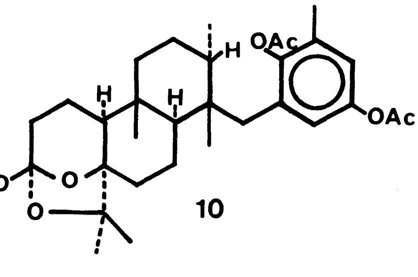

3, R=$<^{\text{OH}}_{\text{H}}$
4, R=O


5, R=H
6, R=OH

In an attempt to trace the natural formation of these compounds this alga is now being studied for its unstable and minor constituents. Freshly-gattered algae were extracted with cold acetone and subjected to a quick succession of chromatographies on silica gel. This study afforded the isolation of nine new compounds among which are included 3-ketotaondiol (2),$^{2)}$ isotaondiol (3),$^{5)}$ and 3-ketoisotaondiol (4).$^{5)}$ We are going to describe here the structure elucidation of two novel peroxylactones (7)$^{6)}$ and (8),$^{7)}$ and the hemilactal triacetate (10)$^{8)}$ based on the


7, R=Ac
8, R=CH_3


9


10

atomaric acid skeleton. The new compounds 7 and 8 were isolated by rapid silica gel column chromatography of the crude extract, while the hemilactal triacetate 10 was isolated by previous acetylation (Ac_2O/Py/25 °C) of the non-resolved and more polar chromatographic fraction. Compounds 7 and 8 were slowly air oxidized to the quinone 9.[9] A limited supply of the crystalline compounds isolated prevented further chemical studies and therefore their structures were solved by single crystal X-ray analysis.

The peroxylactone 7 crystallized in space group $P4_12_12$ with $a = b = 11.216(2)$ and $c = 42.594(8)$ Å with one molecule of composition $C_{29}H_{40}O_6$ forming the asymmetric unit. A total of 2183 unique diffraction maxima were recorded using graphite monochromated CuKα radiation (1.54178 Å) and 1° ω-scans. Of these, 2013 (92%) were judged observed after correction for Lorentz polarization and background effects. A phasing model was achieved by a multisolution tangent formula approach[10] and full matrix least-squares refinements have converged to a current residual of 0.096.[11] Figure 1 is a computer generated perspective drawing of the final X-ray model less hydrogens. The absolute configuration shown is based on biogenetic considerations.

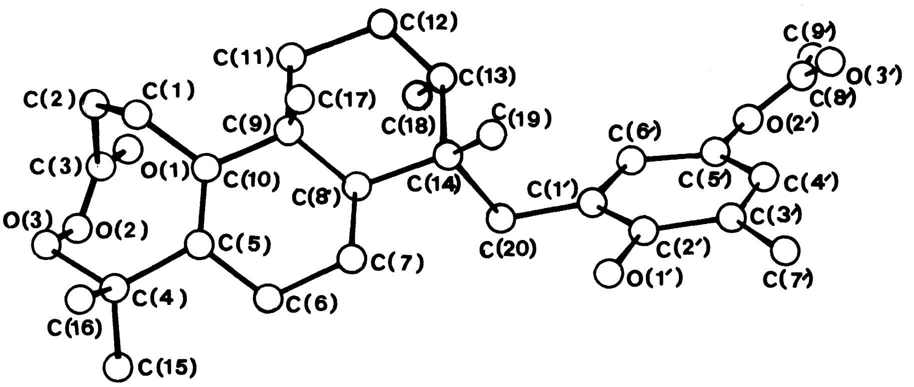


Fig. 1. A computer generated perspective of 7.

The hemilactal triacetate (10) crystallized in the monoclinic space group $P2_1$ with $a = 14.206(4)$, $b = 9.992(2)$, $c = 12.099(3)$ Å and $\beta = 113.44(2)°$ and one molecule of $C_{33}H_{46}O_8$ forming the asymmetric unit. Data were collected as above and 2208 (94%) were judged observed. A phasing model was achieved by a multisolution weighted tangent formula approach[10] and full matrix least squares refinements have converged to a current crystallographic residual of 0.058.[11] Figure 2 is a computer generated drawing of the final X-ray model less hydrogens.

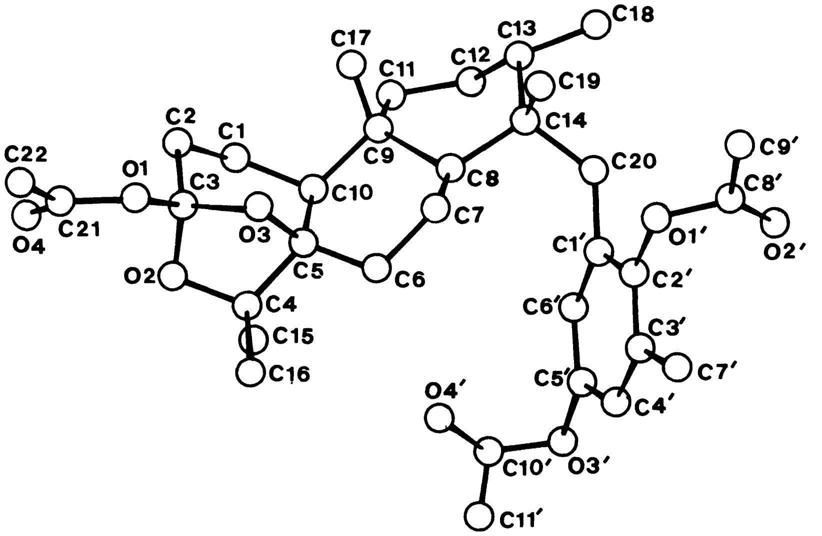
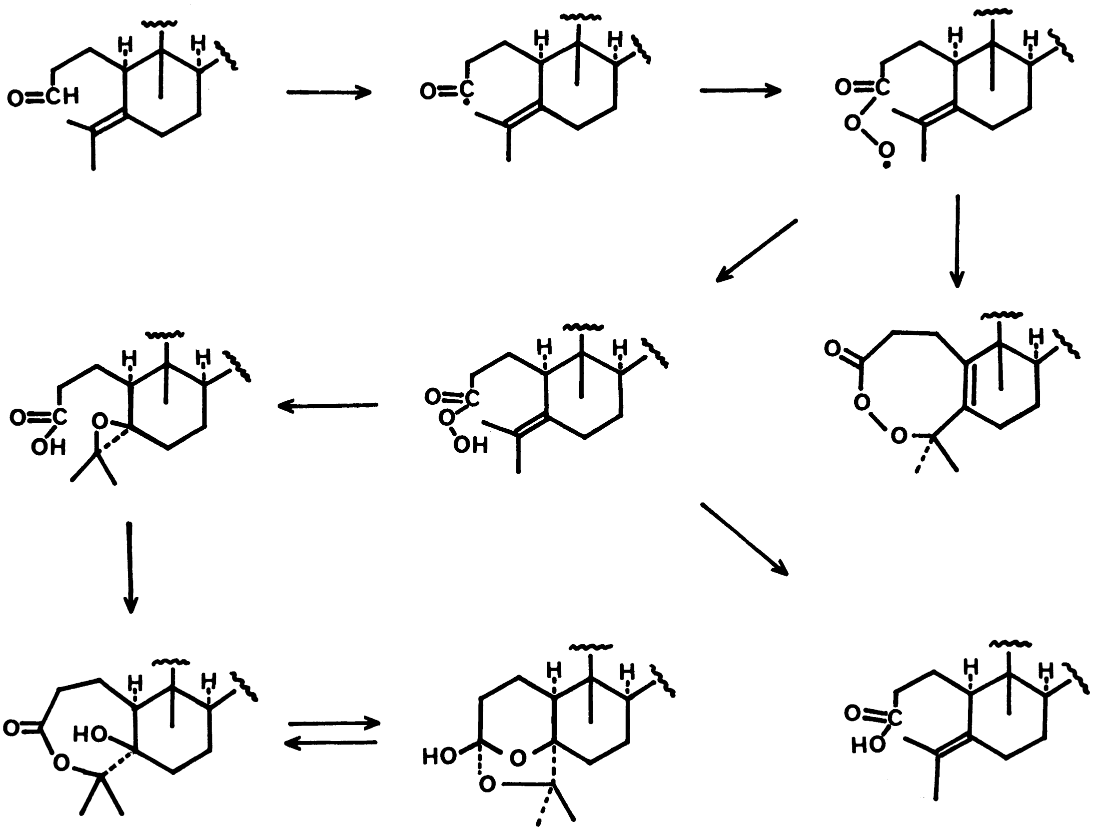


Fig. 2. A computer generated perspective of hemilactal triacetate 10.

Although the aldehyde 5 was not isolated, compounds 7, 8, and 10 are evidence that 5 may be biogenetic precursor and that atomaric acid (6) accounts for the autoxidation of 5 (Scheme 1).



Scheme 1.

This research was supported by Grant No.0153/81 awarded by C.A.I.C.Y.T. (J.D.M.) and by N.I.H. Grant CA-24487 (JC). JR thanks the "Instituto de Cooperación Iberoamericana" for a fellowship.

References

1) Part 28 of "Marine Natural Products of the Atlantic Zone". For Part 27 see: A.G. González, J.D. Martín, C. Pérez, M.A. Ramirez, and F. Ravelo, Tetrahedron Lett., 1981, 5071.
2) A.G. González, J. Darias, J.D. Martín, and C. Pascual, Tetrahedron, 29, 1605 (1973); A.G. González, J.D. Martín, and M.L. Rodríguez, Tetrahedron Lett., 1973 3657; A.G. González, and J.D. Martín, ibid., 1972, 2259; A.G. González, J. Darias, and J.D. Martín, ibid., 1971, 2729.
3) A.G. González, J.Darias, J.D.Martín, and M.Norte, Tetrahedron Lett., 1974, 3951. The stereochemistry of the sec-Me group for atomaric acid previously proposed as β-equatorial should be changed to α-axial in the light of the results obtained in this communication.
4) A.G.González, M.A.Alvarez, J.D.Martín, M.Norte, C. Pérez, and J.Rovirosa, Tetrahedron, 38, 719 (1982).
5) A.G.González, M.A.Alvarez, J.Darias, and J.D.Martín, J. Chem. Soc., Perkin Trans. 1, 1973, 2637.
6) Compound 7, mp 151-152 °C, $\{\alpha\}_D^{27}$ -99°(c 0.14, $CHCl_3$); $C_{29}H_{40}O_6$, M^+ at m/z 484; IR (KBr) 3490, 1760, 1740, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.83 (1H,d,J= 3 Hz), 6.83 (1H,d,J= 3 Hz), 6.71 (1H,d,J= 3 Hz), 4.79 (1H,bs, D_2O exchangeable), 2.23 (3H,s), 2.19 (3H,s), 1.47 (3H,s), 1.28 (3H,s), 1.05 (3H,d,J= 7 Hz), 1.02 (3H,s) and 0.89 (3H,s).
7) Compound 8, mp 133-134 °C, $\{\alpha\}_D^{27}$ -82° (c 0.28, $CHCl_3$); $C_{28}H_{40}O_5$, M^+ at m/z 456; IR (KBr) 3500, 1760, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.68 (1H,d,J= 3 Hz), 6.53 (1H, d,J= 3 Hz), 3.70 (3H,s), 2.19 (3H,s), 1.46 (3H,s), 1.26 (3H,s), 1.07 (3H,d, J= 7 Hz), 1.01 (3H,s) and 0.89 (3H,s).
8) Compound 10, mp 180-181 °C, $\{\alpha\}_D^{27}$ -11° (c 0.31, $CHCl_3$); $C_{33}H_{46}O_8$, M^+ at m/z 570 IR (KBr) 1750, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.94 (1H,d,J= 3 Hz), 6.84 (1H,d,J= 3 Hz), 2.29 (3H,s), 2.24 (3H,s), 2.11 (3H,s), 2.05 (3H,s), 1.28 (3H,s), 1.19 (3H,s), 1.05 (3H,d,J= 7 Hz) and 0.87 (3H,s).
9) Compound 9, $C_{27}H_{36}O_5$, M^+ at m/z 440; uv λ_{max}^{EtOH} 257 nm(ε =2500); IR (KBr) 1760, 1655, 1650, 1630, 1607 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.68 (1H,d,J= 3 Hz), 6.56 (1H, dd,J= 3 and 1.5 Hz), 2.03 (3H,d,J= 1.5 Hz), 1.48 (3H,s), 1.30 (3H,s), 1.00 (3H,s), 0.98 (3H,d,J= 7 Hz) and 0.71 (3H,s).
10) The programs used are described in E.Arnold and J. Clardy, J. Am. Chem. Soc., 103, 1243 (1981).
11) Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre.

(Received June 19, 1984)