ISOLATION AND X-RAY STRUCTURAL DETERMINATION OF THREE NEW DITERPENOIDS FROM THE MARINE ALGA TAONIA ATOMARIA<sup>1)</sup>

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

In our studies on nonenzymic interconversions between the compounds taondiol  $(\underline{1})^{2}$  and atomaric acid  $(\underline{6})$ ,<sup>3)</sup> co-existing metabolites in the seaweed <u>Taonia atomaria</u>, 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  $\underline{5}$  was included.<sup>4)</sup>



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),<sup>2)</sup> isotaondiol (3),<sup>5)</sup> and 3-ketoisotaondiol (4).<sup>5)</sup> We are going to describe here the structure elucidation of two novel peroxylactones  $(7)^{6}$  and (8),<sup>7)</sup> and the hemilactal triacetate  $(10)^{8}$  based on the



atomaric acid skeleton. The new compounds  $\underline{7}$  and  $\underline{8}$  were isolated by rapid silica gel column chromatography of the crude extract, while the hemilactal triacetate  $\underline{10}$ was isolated by previous acetylation (Ac<sub>2</sub>O/Py/25 °C) of the non-resolved and more polar chromatographic fraction. Compounds  $\underline{7}$  and  $\underline{8}$  were slowly air oxidized to the quinone  $\underline{9}$ .<sup>9)</sup> 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  $\underline{7}$  crystallized in space group  $P4_{1}2_{1}^{2}$  with  $\underline{a} = \underline{b} = 11.216$ (2) and  $\underline{c} = 42.594(8)$  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 CuKa radiation (1.54178 Å) and 1°  $\omega$ -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<sup>10</sup> and full matrix least-squares refinements have converged to a current residual of 0.096.<sup>11</sup> 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 (<u>10</u>) crystallized in the monoclinic space group P2<sub>1</sub> with <u>a</u> = 14.206(4), <u>b</u> = 9.992(2), <u>c</u> = 12.099(3) Å and ß = 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<sup>10</sup> and full matrix least squares refinements have converged to a current crystallographic residual of 0.058.<sup>11</sup> Figure 2 is a computer generated drawing of the final X-ray model less hydrogens.

1650



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.

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- 3) A.G. González, J.Darias, J.D.Martín, and M.Norte, Tetrahedron Lett., <u>1974</u>, 3951. The stereochemistry of the sec-Me group for atomaric acid previously proposed as  $\beta$ -equatorial should be changed to  $\alpha$ -axial in the light of the results obtained in this communication.
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- 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<sub>3</sub>);  $C_{29}H_{40}O_6$ , M<sup>+</sup> at m/z 484; IR (KBr) 3490, 1760, 1740, 1600 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) & 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<sub>2</sub>O 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 <u>8</u>, mp 133-134 °C,  $\{\alpha\}_{D}^{27}$ -82° (c 0.28, CHCl<sub>3</sub>);  $C_{28}H_{40}O_5$ , M<sup>+</sup> at m/z 456; IR (KBr) 3500, 1760, 1610 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) & 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 <u>10</u>, mp 180-181 °C,  $\{\alpha\}_{D}^{27}$ -11° (c 0.31, CHCl<sub>3</sub>);  $C_{33}H_{46}O_8$ , M<sup>+</sup> at m/z 570 IR (KBr) 1750, 1740 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) & 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 <u>9</u>,  $C_{27}H_{36}O_5$ , M<sup>+</sup> at m/z 440; uv  $\lambda_{max}^{EtOH}$  257 nm( $\varepsilon$  =2500); IR (KBr) 1760, 1655, 1650, 1630, 1607 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  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.

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