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TAONIANONE, A NEW DITERPENE FROM THE BROWN ALGA *TAONIA AUSTRALASICA*

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Summary. Taonianone, a diterpene with a novel carbocyclic ring system has been isolated from the brown alga *Taonia australasica*.

The only previous report of a chemical investigation of the brown algal genus *Taonia* was that of the isolation of taondiol (1) and atomaric acid (2) from the Atlantic seaweed *Taonia atomaria*[1]. We now report the isolation of taonianone (3), the first representative of a new class of monocarbocyclic diterpenes, from *Taonia australasica* collected near Sydney.

Extraction of the freeze-dried alga with dichloromethane gave a 2% extract from which taonianone (3) was isolated as an oil $[\alpha]_D^{21}$ +12.4° [C, 0.5 in $CHCl_3$] in 65% yield by chromatography on silica gel. Complete spectral information is given below[2].

The formula $C_{20}H_{28}O_2$ was established for taonianone (3) by high resolution mass spectrometry. The molecular ion at m/e 300 (13%) was accompanied by significant fragment ions at m/e 152 (15), 151 (7), 150 (7), 149 (10), 135 (29), 110 (22) and 81 (100%). The presence of a β-substituted furan in (3) was indicated by the 'H n.m.r. spectrum which showed broad one proton resonances at δ 7.27, 7.16 and 6.23 respectively. The partial structure (4) could be written from a combination of 'H n.m.r., ^{13}C n.m.r. and mass spectral evidence. The 'H n.m.r. showed resonances at δ 5.16 (1H, bt *J* 7Hz) and 1.63 (3H, bs, sharpened by irradiation at δ 5.16) and the ^{13}C n.m.r. showed resonances, due to a β-substituted furan at δ 142.6 (d), 138.8 (d), 124.7 (s) and 110.9 (d) and an *E*-CH_2-CH=C(Me)-group [δ 134.5 (s), 124.7 (d)]. The mass spectral fragments at m/e 81, 135 and 149 were also typical of partial structure (4)[3].

The presence of a 2,3,4-trisubstituted *cyclo*pent-2-en-1-one in (3) was suggested by the u.v. spectrum (λ_{max} 232, ε 16,000), the i.r. spectrum (ν_{max} 1700 cm^{-1}) and the ^{13}C n.m.r. spectrum [δ 209.3 (s), 175.4 (s) and 137.1 (s)][4]. The nature of the substituents around the *cyclo*pentenone ring was established by 'H n.m.r. measurements after incremental additions of $Eu(fod)_3$ to a $CDCl_3$ solution of (3). The 'H n.m.r. spectrum of (3) containing 0.5 molar $Eu(fod)_3$ is given below[2] and the magnitude of downfield shifts of separate protons was entirely consistent with the proposed structure (C5-H_A > C6-H_3 > C5-H_B > C4-H > C16-H > C7-H_2 > C19-H_3 > C20-H_3). Also decoupling experiments allowed the assignment of all resonances.

Acknowledgement

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References

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   b) A.G. Gonzalez, J. Darias, J.D. Martin and M. Norte, Tetrahedron Lett., 3951 (1974).
2. 'H n.m.r. spectrum: δ ($CDCl_3$) 7.27 (1H, m), 7.16 (1H, m), 6.23 (1H, bs), 5.16 (1H, bt, *J* = 7Hz), 2.80 (1H, m), 1.68 (3H, s), 1.63 (3H, s), 1.02 (3H, d, *J* = 7Hz), 0.61 (3H, d, *J* = 7Hz). 'H n.m.r. spectrum with 0.5 mol Eu $(fod)_3$:- δ ($CDCl_3$) 7.40 (1H, bs), 7.32 (1H, bs), 6.35 (1H, bs), 5.56 (1H, bt, *J* = 7Hz), 5.38 (1H, dd, *J* = 18, 6.5 Hz), 6.15 (1H, dd J=18, 1.5 Hz), 4.25 (1H, m), 3.62 (3H, s), 3.35 (1H, m), 2.78 (2H, m), 2.50 (4H, m), 2.40 (2H, m), 1.93 (3H, s), 1.38 (3H, d, *J* = 7Hz), 1.36 (3H, d, *J* = 7Hz). ^{13}C n.m.r. spectrum: δ ($CDCl_3$) 209.3 (s), 174.4 (s), 142.6 (d), 138.8 (d), 137.1 (s), 134.5 (s), 124.7 (d), 124.7 (s), 110.9 (d), 45.9 (d), 37.0 (t), 34.8 (t), 28.4, 27.7, 27.5, 24.9, 21.9, 16.0, 14.7, 8.0. I.r. (film): ν_{max} 1700, 1640, 1400, 1380, 1020, 865 cm^{-1}.
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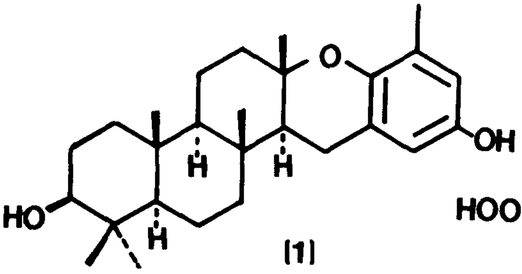

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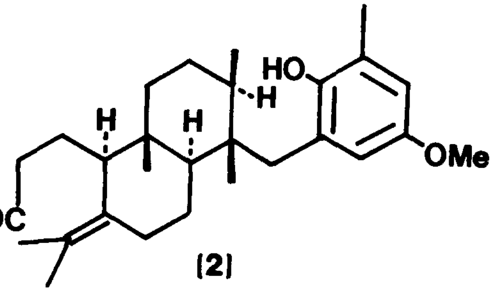

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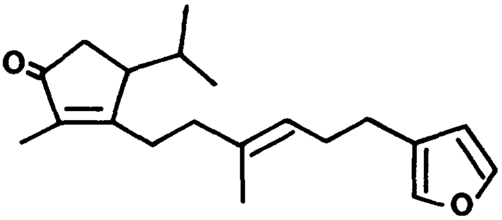
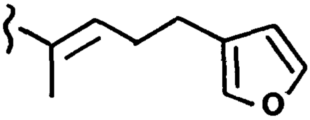


(3)



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