Tetrahedron Letters,Vol.27,No.28,pp 3279-3280,1986
Printed in Great Britain

0040-4039/86 $3.00 + .00
Pergamon Journals Ltd.

SYNTHESIS OF $\Delta^{9(12)}$-CAPNELLENE-8β,10α-DIOL FROM SOFT CORAL *CAPNELLA IMBRICATA*

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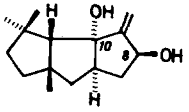
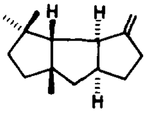
Summary: The first total synthesis of the unusual capnellenediol(1), found in the soft coral *Capnella imbrica*, is described.

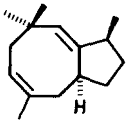
$\Delta^{9(12)}$-Capnellene-8β,10α-diol(1) co-occurs with related alcohols and acetates, in addition to the hydrocarbons $\Delta^{9(12)}$-capnellene(2) and precapnelladiene(3), in the soft coral *Capnella imbricata*[1]. Both (2) and (3) are presumed biogenetic precursors of (1). The capnellenediol(1) shows a novel and unusual ene-diol functionality associated with ring C, which is also found in related capnellene alcohols, isoamijiol, and artolide[2]. Although a number of syntheses of the hydrocarbons capnellene(2) and precapnelladiene(3) have now been published[3], hitherto only a synthesis of the 8-epimer of the capnellenediol(1) has been described[4]. In this *Letter* we report the first synthesis of natural capnellene-8β,10α-diol(1) which features regiospecific displacement of the mesylate derived from (4) using superoxide.



(1)

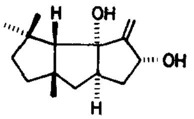


(2)



(3)

i, MsCl
ii, KO_2



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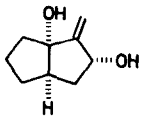

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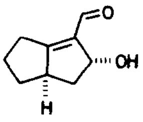

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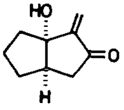

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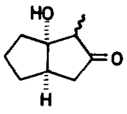

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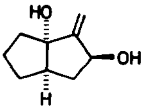

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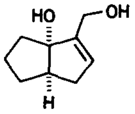

(10)

Our previous work[4] had permitted a flexible synthesis of the capnellene carbon framework, which at the same time accommodated the novel enediol functionality in capnellenediol(1) with the 8α,10α-relative configuration, i.e.(4). Inversion of the 8α-configuration in the sensitive enediol system proved particularly difficult, made more so by the ease with which either of its allylic portions suffered transposition under a range of reaction conditions. Thus, the model enediol(5), for example, provided only the unsaturated aldehyde(6) on attempted oxidation to (7) with chromium based oxidants. In addition, although (5) could be oxidised to (7) using periodinane[5], the reduction of (7) with diisobutylaluminium hydride produced predominantly (8). The Mitsunobu method, and procedures based on caesium acetate[6], proved impractical for inversion of the secondary alcohol residue in (4), but eventually we found success with the much under-used procedure based on nucleophilic displacement with superoxide[7]. Although this method led to a mixture of (9) and (10) with the model enediol(5), displacement of the mesylate derived from (4) with potassium superoxide in 18-crown-6 was totally specific producing the capnellene-8β,10α-diol(1)(40%) as colourless crystals, m.p. 155-6°C. The synthetic capnellene-8β, 10α-diol did not separate from naturally derived material in mixed t.l.c., and the two samples showed completely superimposable p.m.r., and c.m.r. spectra, in addition to mass spectroscopic data.[8]

We thank Professor Braekman who kindly provided a sample of natural $\Delta^{9(12)}$-capnellene-8β,10α-diol, and the SERC for studentships (to M.L. and S.J.T.).

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8. Satisfactory spectroscopic data, together with microanalytical and/or mass spectroscopic data were obtained for all new compounds.

(Received in UK 26 March 1986)