

CAPNELLANE - A NEW TRICYCLIC SESQUITERPENE SKELETON

FROM THE SOFT CORAL CAPNELLA IMBRICATA ^(1,2)

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During our continuing search for terpenoids from marine invertebrates, methylene chloride extracts of sun-dried colonies of the soft coral *Capnella imbricata* (Quoy and Gaimard, 1833) (Coelenterata, Octocorallia), collected off Serwaru, Leti Island, Indonesia, were subjected to repeated silica gel column chromatography, yielding a variety of compounds. We wish to report here on the structure (II) of the most abundant one which is based on the hitherto unknown skeleton (I) for which we have coined the name capnellane.

Compound II, mp. 114-7°; $[\alpha]_D^{CHCl_3} +2^\circ$ (c 0.31); M^+ 252, $C_{15}H_{24}O_3$; ir (KBr) 3400 cm^{-1} (OH), 1640 cm^{-1} ($>C=CH_2$); nmr (60 MHz) $CH_3-\overset{|}{C}-$ 1.01, 1.20, 1.28 (s, 3H each), $>CH-OH$ 4.10 (dd, J 6.5 and 11.0 Hz, 1H), $>CH-OH$ 4.83 (m, 1H), $>C=CH_2$ 5.38 (d, J 1.5 Hz, 2H), furnished a diacetate (III), mp. 91°; M^+ -66 = 276, $C_{19}H_{28}O_5$; ir (film) 3500 cm^{-1} (OH), 1745 cm^{-1} (C=O); nmr CH_3 0.93, 1.21, 1.30 (s, 3H each), $>C=CH_2$ 5.53 (d, J 2Hz, 2H), $>CH-OAc$ 5.10 (dd, J 7.0 and 10.0 Hz, 1H), CH_3COO 2.05 (s, 6H) and a dihydro derivative (PtO₂-ethyl acetate) (IV), mp. 132-3°; M^+ 254, $C_{15}H_{26}O_3$; nmr $CH_3-\overset{|}{C}-$ 1.21, 1.23, 1.31 (s, 3H each), $CH_3-CH<$ 1.10 (d, J 7Hz, 3H), $>CH-OH$ 3.80 (m, 2H).

Oxidation of II (MnO₂-chloroform) afforded a conjugated ketone (V), mp. 187-8°; $[\alpha]_D^{dioxane} +75^\circ$ (c 0.08); M^+ 250, $C_{15}H_{22}O_3$; uv $\lambda_{max}^{225} nm$ (ϵ 5900); ir 1730 cm^{-1} (C=O); nmr $CH_3-\overset{|}{C}-$ 0.90, 1.21, 1.33 (s, 1H each), $>CHOH$ 4.10 (m, 1H), $>C=CH_2$ 5.57, 6.20 (s, 1H each). The ¹³C nmr spectrum ⁽⁶⁾ of II indicates the presence of two sp² carbons (161.54 ppm, $>C=$; 109.12 ppm, $CH_2=$), one allylic secondary carbinol carbon (81.36 ppm) but most importantly an allylic quaternary carbon bearing a hydroxyl group (89.8 ppm). All these data show that II contains one secondary and one tertiary hydroxyl group and three rings, one of which is five membered (see uv and ir ⁽⁷⁾ of V) and carries an exocyclic methylene and one allylic secondary hydroxyl group.

Li/NH₃ reduction of V furnished the β-hydroxy ketone (VI), mp.160-2°; $[\theta]_{295}^{\text{MeOH}} +1062$; $M^+ 252$, C₁₅H₂₈O₃; nmr CH₃-C¹- 1.07, 1.15, 1.32 (s, 3H each), CH₃-CH< 1.07 (d, *J* 7 Hz, 3H), >CH-OH 4.30 (dd, 1H) which on base treatment provided the α:β unsaturated ketone (VII), oil; $M^+ 234$, C₁₅H₂₂O₂; uv (MeOH) λ_{max} 242.5 nm (ε 12,200); ir (CHCl₃) 3450 cm⁻¹ (OH), 1695 cm⁻¹ (C=O), 1655 cm⁻¹ (>C=C<); nmr CH₃-C¹- 0.86, 1.14, 1.30 (s, 3H each), CH₃-C=C 1.71 (d, *J* 2 Hz, 3H), >CH-OH 4.12 (dd, 1H). Evidence for the structure of the α:β unsaturated ketone as shown in VII could be obtained by examining its nmr spectrum (fig.1) on gradual addition of Eu(DPM)₃ shift reagent. At a concentration of 21 mg of Eu(DPM)₃ for 12-15 mg of VII in deuteriochloroform, the nmr spectrum, C_{13,14,15}H₃ 2.26, 2.80, 5.24 (s, 3H each), C₁₂H₃ 3.74 (d, *J* 2Hz), H_e 3.11 (dd, *J*_{ed} = *J*_{eg} 12Hz), H_k 4.02 (dd, *J*_{kj} 18Hz, *J*_{kg} 2Hz), H_j 4.36 (dd, *J*_{jk} 18Hz, *J*_{je} 5.5Hz), H_g 5.04 (m), H_f 5.11 (s), H_d 5.50 (dd, *J*_{de} 12Hz, *J*_{dg} 4 Hz), H_c 5.83 (dd, *J*_{cb} 13Hz, *J*_{ca} 6Hz), H_b 7.16 (dd, *J*_{bc} 13Hz, *J*_{ba} 11 Hz) and H_a 12.25 (dd, *J*_{ab} 11 Hz, *J*_{ac} 6 Hz) was completely resolved and nearly first order so that the interrelationship of all hydrogens could be established by decoupling experiments. Irradiation of carbinol methine H_a collapsed the H_b and H_c signals to a pair of doublets (*J* 13 Hz). Irradiation of H_d simplified the H_e signal to a doublet (*J* 12 Hz). Irradiation of the broad signal H_g transformed the H_k, H_j, H_e and H_d signals to doublets (*J*_{jk} 18Hz, *J*_{de} 12Hz) and sharpened the C₁₂ methyl to a singlet.

The structure and absolute configuration of II were independently established by single crystal X-ray diffraction (crystal data : transparent plates, space-group P₂₁; $\underline{a} = 11.939$, $\underline{b} = 14.766$ and $\underline{c} = 8.316$ Å, $\gamma = 95.74^\circ$, $Z = 4$) using a P 1100 automatic Philips diffractometer.

As will be reported in a subsequent communication *Capnella imbricata* contains additional sesquiterpenes based on the capnellane skeleton (I). In order to avoid the introduction of trivial names, we use the numbering for capnellane outlined in (I) ; (II) is therefore Δ⁹⁽¹²⁾-capnellene-3β,8β,10α-triol. Biogenetic implication of this novel skeleton will be discussed elsewhere together with the structure elucidation of other members of this class.

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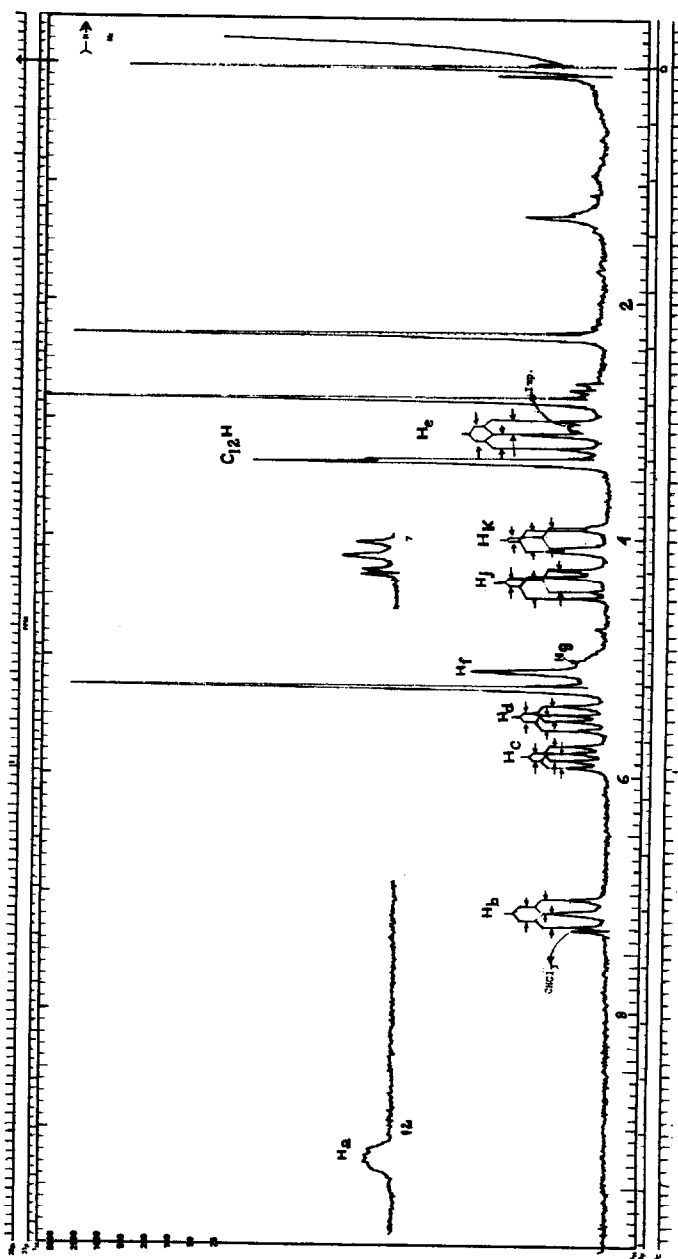
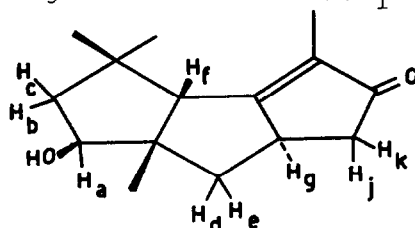
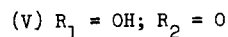
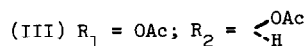
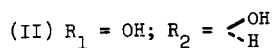
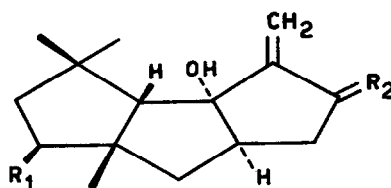
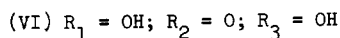
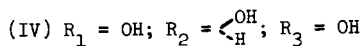
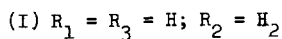
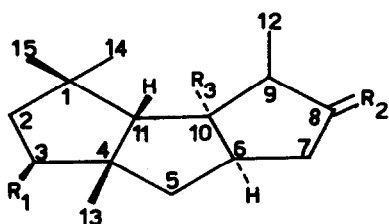


Figure 1. 100 MHz nmr spectrum of compound VII (12-15 mg) after addition of $Eu(DPM)_3$ (21 mg).



(VII)

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4. Chargé de Recherches du Fonds National de la Recherche Scientifique.
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6. Recorded at Stanford University by Hanne Eggert to whom we express our thanks.
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