Tetrahedron Letters No. 19, pp 1671 - 1674, 1978. 0040-4039/78/0501-1671. $02.00/0.

TERPENOIDS LXXV.[1] $\Delta^{9(12)}$-CAPNELLENE, A NEW SESQUITERPENE HYDROCARBON FROM THE SOFT CORAL CAPNELLA IMBRICATA

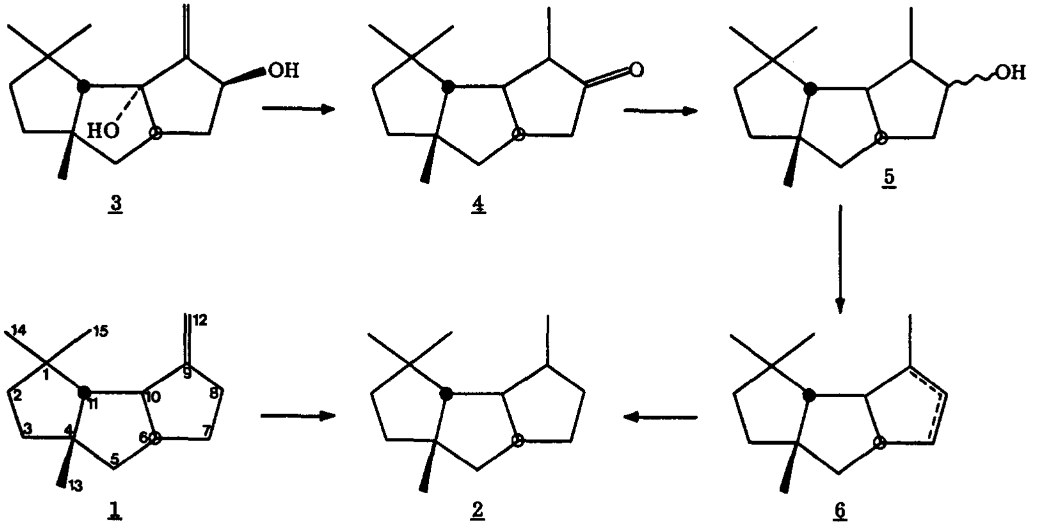
Eser Ayanoglu, T. Gebreyesus, C. M. Beechan and Carl Djerassi*
Department of Chemistry, Stanford University, Stanford, CA 94305
and
M. Kaisin
Collectif de Bio-écologie, Unité de Chimie Bio-organique
Université Libre de Bruxelles, B-1050 Bruxelles, Belgium

(Received in USA 20 January 1978; received in UK for publication 23 March 1978)

A number of novel sesquiterpene alcohols[2-5] have been isolated from the soft coral Capnella imbricata (Quoy and Gaimard, 1833) (Coelenterata, Anthozoa, Alcyonaria, Alcyonacea). We now wish to report the isolation (from the same animal) and structure elucidation of a new sesquiterpene hydrocarbon, $\Delta^{9(12)}$-capnellene (1), which may be the biogenetic precursor of this class of sesquiterpene alcohols.

Column chromatography of the hot pentane extract through silica gel afforded the sesquiterpene hydrocarbons with partial resolution in the hexane fractions. Preparative gas chromatography (12% OV-17, 160°C) gave compound 1: $[\alpha]_D^{20°}$ -145°(c 0.4, $CHCl_3$); MS (70 e.v.) M^+ 204 (11) $C_{15}H_{24}$, 189 (14), 148 (16), 135 (32), 133 (25), 109 (32), 91 (36), 80 (100); IR (neat) 2935, 1453, 1380, 1369, 1361, 870 cm^{-1} (exocyclic methylene); ^1H NMR (100 and 360 MHz, δ, $CDCl_3$), 0.98, 1.08, 1.16 (s, 3H each, tertiary methyls), 4.82 and 4.94 (broad singlets, 1H each, exocyclic methylene); ^{13}C NMR (ppm, $CDCl_3$) three CH_3 (26.07, 30.84, 31.83), five CH_2 (29.11, 31.56, 40.63, 41.73, 48.00), one CH_2= (105.08), three CH (46.07, 52.34, 69.12), one C= (158.75) and two C (42.37, 53.39). These values are in close similarity with the values obtained for capnellane alcohols,[2,3] with the exception of those carbons bearing oxygen atoms. The spectral data obtained are consistent with a tricyclic skeleton which contains a gem dimethyl, a tertiary methyl and an exocyclic methylene group.

Hydrogenation of 1 (Pd/C,rt,7 hrs) yielded 2 as the major component, M^+ 206 (24), $C_{15}H_{26}$, 191 (18), 178 (8), 163 (12), 150 (38), 135 (71), 109 (58), 107 (52), 95 (78), 94 (73), 93 (71), 81 (100); ^1H NMR (100 MHz, $CDCl_3$), 0.91, 1.00, 1.19 (s, 3H each, tertiary methyls), 0.93 (d, J 5.4 Hz, secondary methyl). The minor component, which is most likely a stereoisomer of 2 at C-9, has a slightly longer retention time on GC and has a mass spectral pattern identical to that of 2, except for some intensity differences: M^+ 206 (23), 191 (11), 178 (5), 163 (8), 150 (29), 135 (85), 95 (30), 94 (58), 93 (61), 81 (100).



As a working hypothesis, we assumed that the hydrocarbon 1 was based on the same tricyclic capnellane skeleton (2) as had been established rigorously[2-5] for the corresponding alcohols (e.g. 3). This assumption was confirmed by partial synthesis in the following way: $\Delta^{9(12)}$-capnellene-8β,10α-diol (3)[3] was hydrogenated (Pd/C,rt,48 hrs). This reaction afforded a ketone as a major product instead of the expected alcohol and probably arose by hydrogenolysis of the allylic tertiary alcohol followed by double bond migration. This ketone was identified as 9ξ,10ξ-capnellan-8-one (4) which has spectral data identical with that of the same compound synthesized in our laboratory[3] by another pathway: M^+ 220 (37), 205 (9), 151 (39), 150 (43), 149 (46), 121 (37), 109 (89), 107 (61), 93 (100); IR ($CHCl_3$) 1725 cm^{-1} (C=O); CD $[\theta]_{297}$ +5104; ^1H NMR (100 MHz, $CDCl_3$) 0.96, 1.07, 1.23 (s, 3H each, tertiary methyls), 1.07 (d, J 6.5, secondary methyl). Lithium aluminum hydride reduction of 4 furnished the corresponding alcohol (5): M^+ 222 (2), $C_{15}H_{26}O$, 204 (8), 189 (7), 178 (6), 161 (10), 149 (74), 133 (38), 119 (27), 109 (59), 93 (87), 81 (100); IR ($CHCl_3$) 3450 (OH); ^1H NMR (100 MHz, $CDCl_3$), 0.92, 0.99, 1.18 (s, 3H each, tertiary methyls), 1.03(d, J 8.2 Hz, secondary methyl).

Dehydration ($POCl_3$/pyr,rt,4 days) of 5 gave two peaks upon GC analysis (3% OV-25, 100° C) with very close retention times. The GC/MS (M^+ 204 for each peak) and ^1H NMR (olefinic protons between 5.04 and 5.48 ppm) data showed that these are olefinic hydrocarbons (6) as expected. The mixture was hydrogenated (Pd/C,rt,5 hrs) yielding 2 as the major product, which had identical Rf, gas chromatographic retention time, mass spectral and nuclear magnetic resonance spectral properties as that of the hydrogenation product of the natural olefinic hydrocarbon 1 isolated from *Capnella imbricata*. The minor product obtained from this hydrogenation and the minor hydrogenation product of 1 also have identical gas chromatographic retention times and mass spectra. These interconversions establish the complete structure and stereochemistry of 1 with the exception of the configuration of C-10, which is assumed solely by biogenetic analogy to the oxygenated analogs.[2-5]

Capnella imbricata contains other sesqui- and diterpene hydrocarbons and alcohols which are under investigation in our laboratories.

Acknowledgements: We wish to express our appreciation to Drs. James Schoolery (Varian

Associates, Palo Alto, CA) and Lois Durham for ^{13}C and ^{1}H NMR studies respectively and to Dr. Gerard Singy for extraction of the animal and initial GC/MS analysis. This work was supported by the National Institutes of Health (GM 06840). Grants from the National Science Foundation (GP 28142 and CHE-77-08810) for use of a 100 MHz NMR spectrometer as well as grants from the National Institutes of Health (RR 00711) and from the National Science Foundation (GP 23633) for use of a 360 MHz NMR spectrometer are also gratefully acknowledged.

REFERENCES

1. For paper LXXV see C. M. Beechan, C. Djerassi and H. Eggert, Tetrahedron, in press.
2. M. Kaisin, Y. M. Sheikh, L. J. Durham, C. Djerassi, B. Tursch, D. Daloze, J. C. Braekman, D. Losman and R. Karlsson, Tetrahedron Letters, 2274 (1974).
3. Y. M. Sheikh, G. Singy, M. Kaisin, H. Eggert, C. Djerassi, B. Tursch, D. Daloze and J. C. Braekman, Tetrahedron, 32, 1171 (1976).
4. Y. M. Sheikh, C. Djerassi, J. C. Braekman, D. Daloze, M. Kaisin, B. Tursch and R. Karlsson, Tetrahedron, 33, 2115 (1977).
5. R. Karlsson, Acta Crystallogr., Sect. B, 32, 2609 (1976).