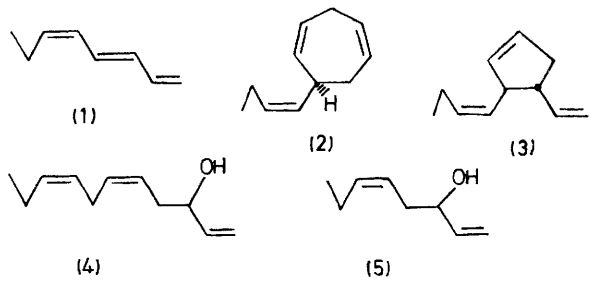
Isolation of (3*S*)-*cis*-Octa-1,5-dien-3-ol from *Chondrococcus hornemanni* (Rhodophyta)

By FRANK X. WOOLARD, B. J. BURRESON, and RICHARD E. MOORE*
(*Department of Chemistry, University of Hawaii, Honolulu, Hawaii* 96822)

Summary (3*S*)-*cis*-Octa-1,5-dien-3-ol, a possible precursor of the sperm-attracting substance, fucoserratene, produced by the female gametes of the brown alga *Fucus serratus*, is a minor constituent in the essential oil of the red seaweed *Chondrococcus hornemanni*.

MALE gametes (sperm) are attracted to female gametes (eggs) by C_8 and C_{11} hydrocarbons in the sexual phase of the life cycle of dioecious brown seaweeds (Phaeophyta). In the öogamous seaweed *Fucus serratus* (class Cyclosporeae) the sperm attractant is the C_8 hydrocarbon (**1**) (fucoserratene)[1] whereas in the isogamous seaweed *Ectocarpus siliculosus* and the anisogamous seaweed *Cutleria multifida* (class Isogeneratae) the male-attracting substances are the C_{11} hydrocarbons (**2**) (ectocarpene)[2] and (**3**) (multifidene).[3] *cis,cis*-Undeca-1,5,8-trien-3-ol (**4**) has been proposed as a common biogenetic intermediate to both the C_8 and C_{11} hydrocarbons found in brown algae[3] but *cis*-octa-1,5-dien-3-ol (**5**) could also be the precursor of (**1**). To date (**4**) and (**5**) have not been found in brown algae.

Chemotaxis is not involved in the sexual reproduction of the red seaweeds (Rhodophyta) as the male gametes are immotile. In an investigation of the essential oil of the red seaweed *Chondrococcus hornemanni*, however, we have found that (**5**) is a minor constituent. The essential oils of two varieties of *C. hornemanni* from Black Point, Oahu, and from the Halona Blowhole, Oahu, contain about the same



amount of (**5**) (1%), but show different halogenated monoterpenes as the major constituents.[4] Compound (**5**), a colourless optically active oil, $[\alpha]_D$ −8° (*c* 0·5, CH_2Cl_2), was isolated by chromatography of the essential oil on silica gel and was eluted with 50% pentane–methylene chloride after chondrocoles A and B.[4] Identification of the dienol as (**5**) was deduced from complete ^1H n.m.r. spectral analysis {δ 0·97 [t, *J* 7 Hz, C(8)-Me], 1·78 (s, OH), 2·18 [quintet, *J* 7 Hz, C(7)-CH_2], 2·31 [t, *J* 6 Hz, C(4)-CH_2], 4·25 [quartet, *J* 6 Hz, C(3)-H], 5·06 [dt, *J* 10, 2 Hz, C(1)-H], 5·20 [dt, *J* 17, 2 Hz, C(1)-H], 5·5 [m, C(5)-H and C(6)-H], 5·85 [ddd,

J 17, 10, 6 Hz, C(2)-H]} and confirmed by synthesis. Hex-1-en-5-yn-3-ol,[5] as the tetrahydropyran (THP) derivative, was converted into the sodium salt with $NaNH_2$ in liquid NH_3 and then alkylated with EtI. Hydrolysis of the resulting THP derivative of oct-1-en-5-yn-3-ol with methanolic HCl followed by catalytic hydrogenation (Lindlar catalyst, ether, 0°) afforded racemic (**5**) which had a ^1H n.m.r. spectrum identical to that of the natural product. The absolute configuration of a natural product (**5**) was shown to be *S* by catalytic hydrogenation to L-(3*R*)-octan-3-ol.[6] No C_8 hydrocarbons were found in the essential oil.

Alk-1-en-3-ols are fairly widespread in both animals and plants. Oct-1-en-3-ol and the corresponding ketone are responsible for the odour of the cultivated mushroom *Agricus bisporus*[7] and the mushroom and metallic flavours of oxidized dairy products.[8,9] Pent-1-en-3-ol and pent-1-en-3-one have also been shown to contribute to the deteriorated flavours of oxidized dairy products.[10] Various precursors have been proposed for the formation of alk-1-en-3-ols, such as a hydroperoxide of linoleic or arachidonic acid for oct-1-en-3-ol,[9] and a hydroperoxide of linolenic acid for pent-1-en-3-ol.[10] Although undec-1-en-3-ols have not been found in brown algae, the related compounds undec-1-en-3-one and (−)-*cis*-3-acetoxyundec-5-enyl thioacetate have been isolated from Hawaiian *Dictyopteris* (Phaeophyta),[11] a seaweed rich in both C_{11} hydrocarbons[12] and unsaturated fatty acids. We predict that cyclization of the 3*S* enantiomer rather than the 3*R* enantiomer of (**4**)[13] leads to dictyopterene B[12] [(−)-(1*R*,2*R*)-*trans*-1-(*trans*,*cis*-hexa-1′,3′-dienyl)-2-vinylcyclopropane], (**2**) [12] (either by direct cyclization or by a concerted Cope rearrangement of dictyopterene C [14]), and multifidene [absolute configuration is tentatively (**3**)].

We thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support, and Mitchell D. Hoyle for identification of the seaweed.

(*Received, 7th April* 1975; *Com.* 412.)

[1] D. G. Müller and L. Jaenicke, *F.E.B.S. Letters*, 1973, **30**, 137; L. Jaenicke and K. Seferiadis, *Chem. Ber.*, 1975, **108**, 225.
[2] D. G. Müller, L. Jaenicke, M. Donike, and T. Akintobi, *Science*, 1971, **171**, 815.
[3] L. Jaenicke, D. G. Müller, and R. E. Moore, *J. Amer. Chem. Soc.*, 1974, **96**, 3324.
[4] B. J. Burreson, F. X. Woolard, and R. E. Moore, *Tetrahedron Letters*, in the press.
[5] A. Viola and J. H. MacMillan, *J. Amer. Chem. Soc.*, 1968, **90**, 6141.
[6] R. Pappo, P. Collins, and C. Jung, *Ann. New York Acad. Sci.*, 1971, **180**, 64.
[7] D. A. Cronin and M. K. Ward, *J. Sci. Food Agric.*, 1971, **22**, 477; S. M. Picardi and P. Issenberg, *J. Agric. Food Chem.*, 1973, **21**, 959.
[8] W. Stark and D. A. Forss, *J. Dairy Res.*, 1962, **29**, 173.
[9] W. Stark and D. A. Forss, *J. Dairy Res.*, 1964, **31**, 253.
[10] W. Stark, J. F. Smith, and D. A. Forss, *J. Dairy Res.*, 1967, **34**, 123.
[11] P. Roller, K. Au, and R. E. Moore, *Chem. Comm.*, 1971, 503; R. E. Moore, J. Mistysyn, and J. A. Pettus, Jr., *J.C.S. Chem. Comm.*, 1972, 326.
[12] R. E. Moore, J. A. Pettus, Jr., and J. Mistysyn, *J. Org. Chem.*, 1974, **39**, 2201.
[13] Discussed by R. E. Moore at the Symposium on the Chemistry of Essential Oils, 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1973.
[14] J. A. Pettus, Jr. and R. E. Moore, *J. Amer. Chem. Soc.*, 1971, **93**, 3087.