

(Cod = 1,5-cyclooctadiene) or  $\text{Ni}(\eta\text{-2-methallyl})_2$  have failed.

The propensity of some  $d^{10}$  ions, e.g.,  $\text{Ag}^+$ ,  $\text{Au}^+$ , and  $\text{Hg}^{2+}$ , to form two coordination has been ascribed to the large s-p or small d-s separation.<sup>12,13</sup> Among nickel triad  $d^{10}$  systems, two coordination is favored for Pd(0) and Pt(0) in comparison with Ni(0) in this respect.<sup>14</sup> Compared to univalent group Ib metals, e.g.,  $\text{Ag}^+$ , the energy separations *per se* do not appear to be favorable for Pd(0) to assume a small coordination number. Thus the present examples delineate importance of Pauling's electron-neutrality principle<sup>15,16</sup> (apart from steric factors) in governing coordination numbers.

(12) R. S. Nyholm, *Proc. Chem. Soc., London*, 273 (1961).

(13) L. E. Orgel, "An Introduction to Ligand Field Theory," Wiley, New York, N. Y., 1960, p 66.

(14) The d-s separations (eV) are -1.8 ( $\text{Ni}^0$ ), 0.81 ( $\text{Pd}^0$ ), -0.76 ( $\text{Pt}^0$ ), 4.87 ( $\text{Ag}^+$ ), and 1.87 ( $\text{Au}^+$ ), while the s-p separations (eV) are 3.52 ( $\text{Ni}^0$ ), 4.32 ( $\text{Pd}^0$ ), 4.04 ( $\text{Pt}^0$ ), 5.07 ( $\text{Ag}^+$ ), and 5.96 ( $\text{Au}^+$ ). See C. Moore, *Nat. Bur. Stand. (U. S.), Circ., No. 467*, Vol. II, 1952; Vol. III, 1958.

(15) L. Pauling, *J. Chem. Soc.*, 1461 (1948).

(16) R. S. Nyholm, "Proceedings of the Third International Congress on Catalysis," Vol. 1, North-Holland Publishing Co., Amsterdam, 1965, p 25.

M. Matsumoto, H. Yoshioka, K. Nakatsu  
Faculty of Science, Kwansai Gakuin University  
Nishinomiya, Hyogo 662, Japan

T. Yoshida, Sei Otsuka\*

Department of Chemistry, Faculty of Engineering Science  
Osaka University  
Toyonaka, Osaka, Japan

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### Multifidene and Aucantene, $\text{C}_{11}$ Hydrocarbons in the Male-Attracting Essential Oil from the Gynogametes of *Cutleria multifida* (Smith) Grev. (Phaeophyta)

Sir:

Cellular chemotaxis<sup>1</sup> plays a role in the reproduction of brown algae (Phaeophyta); *i.e.*, the gynogametes (eggs) release volatile substances that act as attractants for the androgametes (sperm). In the isogamous seaweed *Ectocarpus siliculosus*, for example, the sex attractant has been identified as (6*S*)-(cis-1'-butenyl)-1,4-cycloheptadiene (ectocarpene, **4**),<sup>2</sup> a compound which is also a constituent of the essential oils from vegetative thalli of *Dictyopteris plagiogramma* and *D. australis*.<sup>3,4</sup> In the oogamous seaweed *Fucus serratus* the male attractant is a 1,3,5-octatriene (fucoserratene).<sup>5</sup> In this communication we wish to report the isolation and structure determination of the male-attracting substance and a related, biologically inactive compound

(1) For recent reviews see (a) L. Jaenicke and D. G. Müller, *Fortschr. Chem. Org. Naturst.*, **30**, 61 (1973); (b) L. Jaenicke, Annual Lecture, Rheinisch-Westfälische Akademie der Wissenschaften, Westdeutscher Verlag, Köln-Opladen, 1972.

(2) D. G. Müller, L. Jaenicke, M. Donike, and T. Akintobi, *Science*, **171**, 815 (1971).

(3) J. A. Pettus, Jr., and R. E. Moore, *J. Amer. Chem. Soc.*, **93**, 3087 (1971).

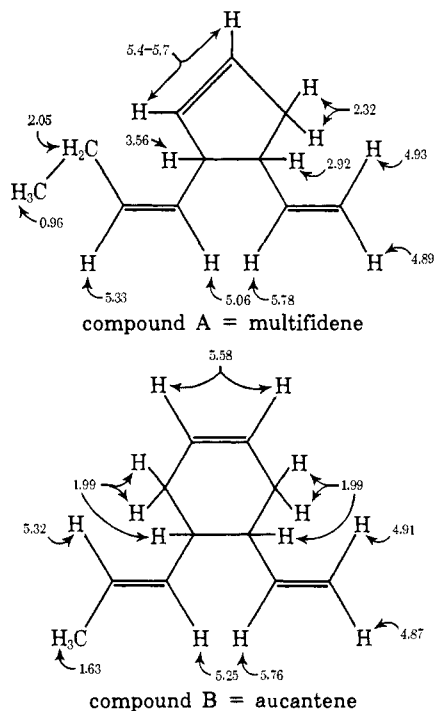
(4) The configuration of C-6 in the Cope rearrangement product of dictyopterene B, (-)-6-(cis-but-1'-enyl)-cyclohepta-1,4-diene, is predominantly R as partial reduction with 1 equiv of diimide produces a small amount of (+)-(S)-6-butyl-cyclohepta-1,4-diene (J. A. Pettus, Jr., Ph.D. Thesis, University of Hawaii, 1971). Dictyopterene D' (ectocarpene) therefore has the S-configuration at C-6.

(5) D. G. Müller and L. Jaenicke, *FEBS (Fed. Eur. Biochem. Soc.) Lett.*, **30**, 137 (1973).

from the anisogamous brown alga *Cutleria multifida* (Smith) Grev. from the Mediterranean coast.

Female plants of *Cutleria multifida* were cultured in the laboratory from unfertilized eggs.<sup>6</sup> Mature plants were placed in flasks (*ca.* 50 g wet weight in 1-l. sterile sea water per flask) and allowed to release the motile macrogametes into the medium every morning continuously for a period of more than 5 months. The macrogametes were separated from the plants each day by decanting the medium and replacing it with fresh sea water. A stream of purified air was then passed through the suspension of female gametes in the decanted sea water for 24 hr and the volatile material was collected in a Dry Ice cooled trap containing 0.3 ml of fluorocarbon FC-78 (bp 50-60°),<sup>7</sup> which dissolved the organic material and separated it from the bulk of the condensed water. Subsequent gas chromatography<sup>8</sup> of this solution on 5% DEGS on Chromosorb P at 65° separated the male-attracting oil into three dextro-rotatory components: 2.5 mg of A, 1.0 mg of B, and 0.2 mg of C from 1 kg of wet seaweed.<sup>9</sup> Bioassay<sup>1,6</sup> showed that compound A was responsible for the positive chemotaxis of the male microgametes; compounds B and C possessed no significant biological activity. Compounds B and C were also found to be constituents of the essential oil from the male and asexual plants of *C. multifida*.

Compounds A, B, and C exhibit mass spectra that



are virtually identical with the mass spectrum of **4**, showing that all three components are  $\text{C}_{11}\text{H}_{16}$  hydrocarbons and structurally related to **4**. Furthermore all three compounds possess three unconjugated double bonds

(6) Male gametes were exposed to vaseline droplets containing the samples. The halo of gametes around such lures, measured against blanks, is indicative of gamone activity: D. G. Müller, *Biochem. Physiol. Pfl.*, in press.

(7) Obtained from 3M Co., Düsseldorf, Germany.

(8) Compounds A, B, and C have the following Kovats indices on a column of 12.5% Apiezone and 2% Igepal on alkali-washed Chromosorb W: 1056.7, 1086.3, and 1165.0, respectively. The latter is identical with the retention value of ectocarpene (1164.7).

(9) Weights were estimated using *n*-nonane as a reference standard.

and a ring as they exhibit only end absorption curves for ultraviolet spectra and are readily hydrogenated catalytically to hexahydro derivatives as shown by mass spectrometry. Compound C is concluded to be **4** as it is dextrorotatory and has an identical gas chromatographic retention time<sup>8</sup> and proton nmr spectrum. The proton nmr spectrum of compound A,  $[\alpha]^{23.5D} +28^\circ$  ( $\text{CCl}_4$ ,  $c$  0.0036), clearly shows the presence of an ethyl group connected to an olefinic methine (triplet at  $\delta$  0.96 and a quintet at  $\delta$  2.05,  $J = 7.5$  Hz) and a vinyl group (doublet of multiplets at  $\delta$  4.89,  $J = 10$  Hz for cis coupling, and a doublet of multiplets at  $\delta$  4.93,  $J = 17$  Hz for trans coupling;  $J_{\text{gem}}$  estimated to be 2.5 Hz). The proton nmr spectrum of compound B,  $[\alpha]^{23.5D} +105^\circ$  ( $\text{CCl}_4$ ,  $c$  0.002), however, shows instead a methyl group connected to an olefinic methine (doublet at  $\delta$  1.63, apparent  $J = 5$  Hz) in addition to a vinyl group (doublet of multiplets at  $\delta$  4.87,  $J_{\text{cis}} = 10$  Hz, and a doublet of multiplets at  $\delta$  4.91,  $J_{\text{trans}} = 17$  Hz,  $J_{\text{gem}}$  again estimated to be 2.5 Hz). These findings, coupled with biogenetic arguments (see below), suggested that compound A is a 4-vinyl-5-(1'-butenyl)cyclopentene and that compound B is a 4-vinyl-5-propenylcyclohexene. Detailed analysis of the proton nmr spectra<sup>10</sup> verified these conclusions and in addition established the stereochemistry of both compounds.

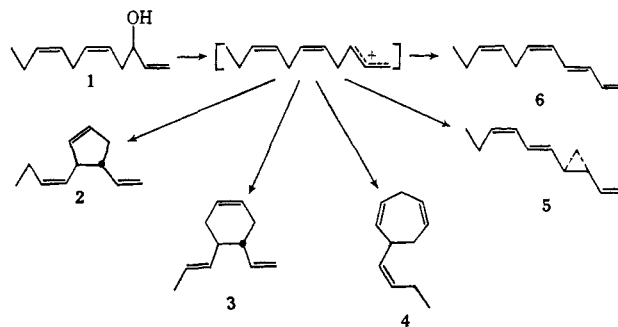
The most salient features of the nmr spectrum of compound A are the following. (1) Long range coupling ( $J = 1$  Hz) in the quintet at  $\delta$  2.92 for the C-4 proton and the doublet of multiplets at  $\delta$  4.89 and 4.93 for the terminal methylene protons shows that the vinyl group is attached to C-4. (2) The triplet of multiplets at  $\delta$  3.56 is assigned to the C-5 methine proton and reflects large vicinal coupling ( $J = 8.5$  Hz) to the C-4 ring protons and the C-1 olefinic proton in the butenyl side chain, a small vicinal coupling ( $J \approx 2$  Hz) to the C-1 ring proton, and long range coupling to several protons. (3) The geometry of the double bond in the butenyl side chain is cis as the C-2' proton which resonates as a doublet of triplets at  $\delta$  5.33 interacts with the C-1' proton, which appears as a doublet of doublets at  $\delta$  5.06, by 11 Hz. Finally, the vinyl and butenyl substituents are tentatively assigned to have a trans relationship.

The nmr spectrum of B, on the other hand, has the following important characteristics. (1) Six protons absorb in a broad multiplet at  $\delta$  1.99 and this signal is attributed to the C-3 and C-6 methylene protons and the axially disposed (therefore trans to each other) C-4 and C-5 methine protons. (2) The geometry of the propenyl side chain is trans, since the C-1' and C-2' proton interaction is 17 Hz as shown in the doublet of quartets for the C-2' proton at  $\delta$  5.32. (3) The chemical shifts of most of the ring protons and vinyl protons are comparable with those of vinyl cyclohexene.<sup>11</sup>

From these data it is clear that compound A is *trans*-4-vinyl-5-(*cis*-1'-butenyl)cyclopentene (**2**) and that compound B is *trans*-4-vinyl-5-(*trans*-1'-propenyl)cyclohexene (**3**). We propose the names multifidene for the

biologically active **2** and aucantene (Latin for "Vogel-sang" where the compounds were isolated first) for the biologically inactive **3**.

The two new hydrocarbons from *Cutleria* are obviously biogenetically related to the  $\text{C}_{11}$  hydrocarbons,<sup>12</sup>  $\text{C}_{11}$  ketones,<sup>13</sup> and sulfur compounds<sup>14</sup> from Hawaiian *Dictyopteris*. *cis,cis*-Undeca-1,5,8-trien-3-ol (**1**) may



serve as a common intermediate<sup>15</sup> since it satisfactorily explains the formation of all the algal  $\text{C}_{11}\text{H}_{16}$  hydrocarbons (**2**, **3**, **4**, **5**,<sup>12b</sup> **6**<sup>12b</sup>) isolated to date, including the  $\text{C}_8$  hydrocarbon fucoserratene.<sup>16</sup>

**Acknowledgment.** We thank Miss E. Fölster for skilled technical assistance and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support.

(12) (a) R. E. Moore, J. A. Pettus, Jr., and M. S. Doty, *Tetrahedron Lett.*, 4787 (1968); (b) J. A. Pettus, Jr., and R. E. Moore, *Chem. Commun.*, 1093 (1970).

(13) R. E. Moore and G. Yost, *J. Chem. Soc., Chem. Commun.*, 937 (1973).

(14) (a) P. Roller, K. Au, and R. E. Moore, *Chem. Commun.*, 503 (1971); (b) R. E. Moore, *ibid.*, 1168 (1971); (c) R. E. Moore, J. Mistysyn, and J. A. Pettus, Jr., *ibid.*, 326 (1972).

(15) 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. See Abstract No. AGFD 056 for a scheme outlining the biogenesis of the  $\text{C}_{11}\text{H}_{16}$  hydrocarbons and certain ketones and sulfur compounds in Hawaiian *Dictyopteris* from *cis*-undeca-1,5-dien-3-ol.

(16) The biogenesis of fucoserratene, a 1,3,5-octatriene,<sup>5</sup> can also be rationalized from **1** if the latter is first oxidized at C-7 to *cis,cis*-undeca-1,5,8-triene-3,7-diol. Subsequent heterolytic fragmentation [C. A. Grob and P. W. Schiess, *Angew. Chem.*, **79**, 1 (1967); *Angew. Chem. Int. Ed.*, **6**, 1 (1967)] then results in acrolein and *trans,cis*- or *cis,cis*-1,3,5-octatriene. Synthetic work [L. Jaenicke and K. Seferiadis, unpublished results] establishes that fucoserratene is *trans,cis*-1,3,5-octatriene.

(17) Work done while on sabbatical leave at the Institut für Biochemie der Universität zu Köln, Germany. Financial assistance from the National Science Foundation (GP 29412) and the donors of the Petroleum Research Fund (5514-AC1), administered by the American Chemical Society, is gratefully acknowledged.

Lothar Jaenicke\*

Institut für Biochemie der Universität zu Köln  
D-5 Köln, Germany

Dieter G. Müller

Max-Planck-Institut für Züchtungsforschung  
D-5 Köln-Vogelsang, Germany

Richard E. Moore<sup>17</sup>

Department of Chemistry, University of Hawaii  
Honolulu, Hawaii 96822

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## Reactive Transition Metal Dinitrosyl Complexes. Synthetic Uses and Catalytic Properties

Sir:

For a variety of reasons, not the least of which are environmental, there is obvious interest in reactions

(10) Proton assignments were confirmed by appropriate spin-spin-decoupling experiments.

(11) The nmr spectra of compound B and 4-vinylcyclohexene were compared directly. We found that chemical shifts for 4-vinylcyclohexene differed slightly with those reported in the Varian High Resolution NMR Spectra Catalog, Vol. I, 1962.