or W^{6+} by direct donation into empty orbitals of the appropriate symmetry. The σ bonding is analogous to that in metallacyclobutanes[7] and will not be discussed further here. There are three π frontier orbitals in $[C_3H_3]^{3-}$, b_2 (bonding), a_2 (nonbonding), and b_2^* (antibonding), of which the first two are occupied. The b_2^* orbital, being very high in energy, does not contribute significantly to any occupied orbitals of $[WC_3H_3]^{3+}$ and may be ignored henceforth. The π interaction will be between the b_2 and a_2 orbitals of $[C_3H_3]^{3-}$ and the available π orbitals on either $[CH]^{3+}$ or W^{6+}; it is the difference in the latter that accounts for the differences between the organic and organometallic systems, as shown qualitatively in Figure 2. In $[CH]^{3+}$ there is one $p\pi$ orbital available, and its interaction with the π orbitals of $[C_3H_3]^{3-}$ leads to the familiar orbital pattern for C_4H_4, in which the HOMO is a half-filled nonbonding e_u orbital (under D_{4h} symmetry). In contrast to the situation in $[CH]^{3+}$, there are two $d\pi$ orbitals in a d^0 metal ion that can interact with the b_2 and a_2 orbitals of $[C_3H_3]^{3-}$. The principle bonding interactions, shown in Figure 3, consist of stabilization of *both* the b_2 and a_2 orbitals of $[C_3H_3]^{3-}$, with concomitant formation of b_2^* and a_2^* antibonding orbitals.

It is apparent that the major difference between the bonding in C_4H_4 and $[WC_3H_3]^{3+}$ is in the HOMO of each. In square C_4H_4, the π orbital of $[CH]^{3+}$ cannot interact with the a_2 orbital of $[C_3H_3]^{3-}$, necessarily leading to the nonbonding HOMO which is characteristic of antiaromatic systems. In $[WC_3H_3]^{3+}$, by contrast, the interaction of one of the $d\pi$ orbitals with the a_2 orbital of $[C_3H_3]^{3-}$ produces a strongly bonding orbital in which the W is π bonded to the α-carbons (Figure 3). This type of interaction has been anticipated by Thorn and Hoffmann.[8] Mulliken population analysis of the a_2 orbital of $[WC_3H_3]^{3+}$ indicates that it consists of nearly equal contributions from the W $d\pi$ (52%) and the $[C_3H_3]^{3-}$ a_2 (48%) orbitals, and the overlap population between the two (0.350) is sizable. The LUMO of $[WC_3H_3]^{3+}$ is 5.0 eV above the a_2 HOMO, again indicative of the strong stabilization within the a_2 orbital. A fully occupied, strongly π-bonding HOMO in a cyclic system is characteristic of aromatic systems, and despite its being a four-π-electron system, it is tempting to call $[WC_3H_3]^{3+}$ a metalloaromatic system; this concept was first used to rationalize the stability of cyclobutadiene–metal complexes vis-à-vis the instability of cyclobutadiene.[9] As is the case in $(C_4H_4)Fe(CO)_3$, the greater flexibility of d orbitals allows favorable bonding interactions in $[WC_3H_3]^{3+}$ not achievable in the purely organic system C_4H_4. It is also of interest to note that the HOMO stabilization evident in metallacyclobutadiene complexes is not possible in dimetallacyclobutadiene complexes wherein there are no C–C nonbonding orbitals to stabilize.[10]

The analysis of $[WC_3H_3]^{3+}$ also accounts for the anomalously short W–C_β distance in the tungstenacyclobutadiene system.[3] The b_2 orbital of $[C_3H_3]^{3-}$, which has its largest contribution (48%) from the β-carbon, interacts strongly with the $d\pi$ orbital which is spatially directed toward it (Figure 3). This results in the b_2 orbital of $[WC_3H_3]^{3+}$ having an 18% contribution from the W $d\pi$ orbital. Thus, the β-carbon is pulled toward the W center by an across-the-ring interaction. The MO calculation of Cl_3W-C_3H_3[11] indicates that the LUMO of the complex, which is 4.2 eV above the HOMO, is essentially the b_2^* orbital of $[WC_3H_3]^{3+}$, i.e., the antibonding counterpart of the across-the-ring bond. It is expected, therefore, that a d^1 or d^2 metallacyclobutadiene complex would have an appreciably reduced interaction between the metal center and the β-carbon relative to the d^0 system; it is noted that two late-transition-metal adducts of the triphenylcyclopropenium cation,[12] while possessing metallacyclobutadienoid cores, do not exhibit unusually short M–C_β bonds. Since the M–C_β interaction helps to stabilize the d^0 metallacyclobutadiene, an undesirable situation if it is the catalytic intermediate in acetylene metathesis, it may be the case that d^1 or d^2 systems will be better catalysts than the d^0 ones.

Acknowledgment. Thanks are due to Professors R. R. Schrock and M. R. Churchill for a preprint of ref 3.

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Pentalenene Biosynthesis and the Enzymatic Cyclization of Farnesyl Pyrophosphate

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Received August 24, 1982

The recognition that farnesyl pyrophosphate (**1**, Scheme I) can serve as a biosynthetic precursor of all cyclic sesquiterpenes, of which nearly 200 individual skeletal types are now known, remains one of the outstanding theoretical triumphs of modern bioorganic chemistry.[2] Until recently, however, few examples had been reported of direct investigations of the key cyclization reactions, the bulk of the experimental evidence for the role of farnesyl pyrophosphate having rested on inference from the results of traditional early-precursor–late-product incorporation experiments.[3] Only in recent years, as attention has turned increasingly to the development of cell-free systems from plants and microorganisms, has it become possible to investigate directly the important and fascinating cyclases that lie at the heart of terpenoid biosynthesis.[4] We report below the preparation of a cell-free extract of *Streptomyces* that catalyzes the cyclization of *trans,trans*-farnesyl pyrophosphate to pentalenene (**2**),[5] the parent hydrocarbon[6] of the pentalenolactone family of sesquiterpene antibiotics.[8]

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(6) The role of pentalenene as a precursor of the more oxidized pentalenanes has been established by feeding experiments with intact cells. The requisite [1,13-^{3}H]pentalenene (**2**; 8.9×10^9 dpm/mmol) was prepared according to ref 5b by the use of ^{3}H-$NaBH_4$ to reduce the mercuric nitrate cyclization product of humulene (**6**). Oxidation of a portion of this labeled pentalenene to the corresponding 13-carboxylic acid methyl ester (**8**) established that 14% of the tritium label was at C-1 (1.3×10^9 dpm/mmol). Feeding of 7.1×10^8 dpm of [1,13-^{3}H]pentalenene to a culture of *Streptomyces* UC5319 gave labeled pentalenolactone (**9**; 0.7% incorporation, 6×10^7 dpm/mmol), pentalenolactone E (**10**; 0.2%, 1.7×10^7 dpm/mmol), pentalenolactone F (**11**;[7] 0.2%, 1.7×10^7 dpm/mmol), and pentalenic acid (**12**; 0.1%, 1.2×10^7 dpm/mmol), each isolated and rigorously purified as the derived methyl ester. The site of labeling was unambiguously confirmed by PCC oxidation of **12** to the corresponding ketone (**13**), which retained ≤1% of the original tritium activity (Scheme III).
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Scheme I

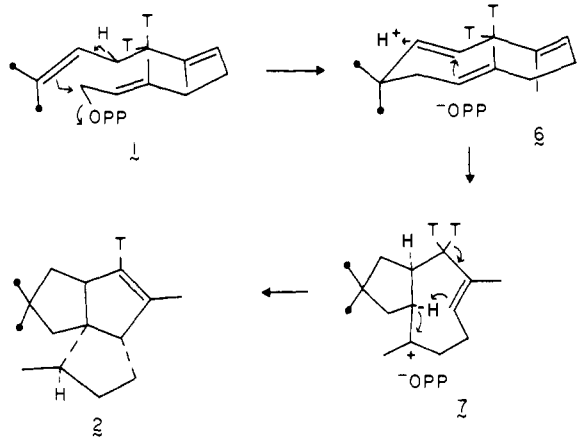


Table I. Conversion of [8-^{3}H; 12,13-^{14}C]Farnesyl Pyrophosphate to Pentalenene and Distribution of the Label

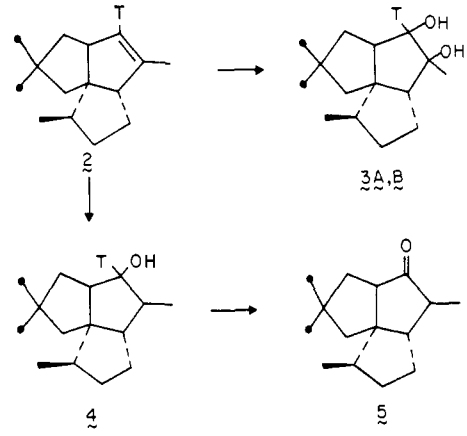
compd	^{14}C specific activity, dpm/mmol	^{3}H/^{14}C
1[a]	5.6×10^7	57.3 ± 1.0[b]
2[c]	1.5×10^4[d]	
3A	1.28×10^4	25.6 ± 0.1
3B	1.29×10^4	25.9 ± 0.2
4	1.06×10^4	26.8
5	1.16×10^4	3.1 ± 0.2

[a] Amount incubated, 1.6×10^7 dpm ^{14}C (29 μmol). [b] Based on recrystallization of farnesyl diphenylurethane. [c] Total recovered activity, 3.3×10^3 dpm ^{14}C. [d] Diluted to 44 mg.

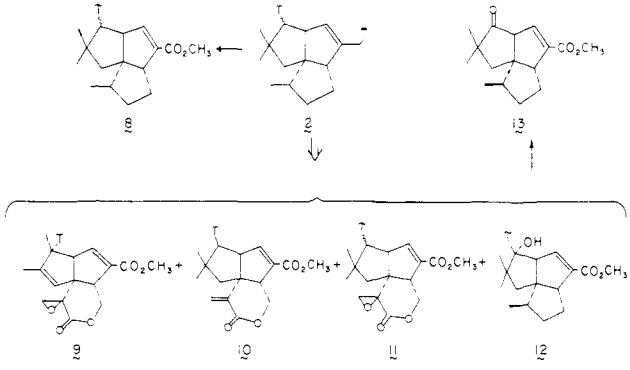
trans,trans-[8-^{3}H]Farnesol was prepared by coupling of 8-chloro[8-^{3}H]geranyl benzyl ether[9] with the lithio anion of dimethylallyl phenyl sulfone,[11a] followed by reductive cleavage with lithium in ethylamine.[10,11b] After addition of [12,13-^{14}C]farnesol, prepared as previously described, a portion of the resulting mixture was converted to farnesyl diphenylurethane,[12] which was recrystallized to constant activity (^{3}H/^{14}C = 57.3:1.0; atom ratio 2:2; Table I). The remaining allylic alcohol was then converted to the corresponding pyrophosphate ester by standard methods.[4c]

For the preparation of the cell-free extract, the mycelium from 2.4 L of a 60-h culture of *Streptomyces* UC5319, grown as previously described,[8] was harvested by centrifugation at 4000g, washed with glass-distilled water and two times each with successive portions of 1.0 M KCl and 0.8 M NaCl,[13] and then suspended in 100 mL of 0.1 M potassium phosphate buffer, pH 7.2, containing 0.4 mM dithioerythritol (DTE), 1.0 mM EDTA, and 5% (v/v) glycerol. The cells were ruptured by rapid stirring for 3 min with 0.1–0.15-mm glass beads in a 250-mL jacketed cell cooled to 0–4 °C. After removal of the glass beads from the broken cell mass by brief centrifugation at 8000*g*, the suspension was further centrifuged for 1 h at 34000*g* to remove cell debris.[14] The resulting supernatant (100 mL, 0.5 mg of protein/mL[15]) was degassed by sparging with nitrogen for 1 min and then incubated immediately in a stoppered flask with 10.0 μmol of [8-^{3}H,12,13-^{14}C]farnesyl pyrophosphate and 10.0 μmol $MgCl_2$. After

Scheme II



Scheme III



1.5 h at 30 °C the reaction was quenched by addition of an equal volume of acetone, and the mixture was extracted with pentanes. Synthetic (±)-pentalenene (**2**,[16] ca. 5 mg, Scheme II) was added as carrier, and the pentane solution, after drying and concentration, was subjected to purification by preparative TLC (silica gel, hexane). The activity of the recovered pentalenene (1.5×10^3 dpm ^{14}C) corresponded to a conversion rate of 0.03 nmol of pentalenene/mg of protein per hour. The above incubation was repeated two more times, leading to the formation of **2** with a total activity of 3.3×10^3 dpm ^{14}C. Control experiments on analogous cell-free preparations established that the rate of pentalenene formation was proportional to the enzyme concentration at 0.1 mM substrate, while prior boiling of the enzyme extract gave only radioinactive pentalenene. The crude enzyme preparations contained significant quantities of competing phosphatase–pyrophosphatase activities and were markedly unstable, losing 50% of the cyclase activity after only 4 h at 4 °C.

So that the specificity of labeling in the enzymatic cyclization could be established, the recovered pentalenene was diluted with additional carrier to a total of 44 mg of **2**, of which 26 mg was converted to the corresponding mixture of diastereomeric *cis*-6,7-diols **3A** and **3B** by treatment with OsO_4 (1.0 equiv/pyridine/18 h/25 °C followed by aqueous $NaHSO_3$; Scheme II). Recrystallization from hexane/CH_2Cl_2 gave 6 mg of the minor isomer, diol **3A**,[17a,b] which was recrystallized to constant activity (mp 145–146 °C). Recrystallization from hexanes of the concentrated mother liquor gave 10 mg of diol **3B**[17a,c] (mp 74.5–75 °C), which was in turn recrystallized to constant activity. Both solid derivatives showed the expected loss of 50% of the original tritium, based on ^{3}H/^{14}C ratio (atom ratio 0.9:2; Table I). The site of tritium labeling in the remaining pentalenene was unam-

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(14) Active preparations could also be obtained by sonication of 30-mL batches of cell suspension for 30-s intervals with intermittent cooling up to a total of 5 min (130 W, 90% duty cycle, 4 °C) or by grinding of the cell paste with Sigma Type 305 alumina (80 g of wet cells/50 g of alumina).

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(16) Prepared according to ref 5b and purified by preparative TLC on 15% silver nitrate impregnated silica gel (R_f 0.37, hexanes).

(17) (a) All new compounds gave satisfactory 250-MHz ^{1}H NMR, 62.8-MHz ^{13}C NMR, and IR data. (b) Calcd for $C_{15}H_{24}O$ ($M^+ - H_2O$) 220.1827, found 220.1841. (c) Calcd for $C_{15}H_{24}O$ ($M^+ - H_2O$) 220.1827, found 220.1822. (d) Calcd for $C_{15}H_{26}O$ 222.1984, found 222.1985. (e) Calcd for $C_{15}H_{24}O$ 220.1827, found 220.1850.

biguously established by hydroboration-oxidation (4.0 equiv of BH_3·THF/THF/1 h/0 °C; 30% H_2O_2/3.0 M NaOH, 1:1/1 h/55 °C) to yield 7-hydroxypentalenane (**4**)[17a,d] as a 20:1 mixture of epimers, followed by oxidation with PCC in CH_2Cl_2 (1 h/25 °C) to give pentalen-7-one (**5**)[17a,e] that was essentially devoid of tritium.

The preceding experiments firmly demonstrate the enzymatic conversion of farnesyl pyrophosphate to pentalenene and are consistent with the pathway illustrated in Scheme I. The proposed cyclization mechanism is further supported by the biomimetically modeled synthesis of pentalenene via cation **7**, reported earlier by Shirahama and Matsumoto,[5b] and used for the preparation of racemic pentalenene in the present study. On the basis of incorporation experiments with intact cells, we have previously suggested on stereochemical grounds that the enzymatic formation and further cyclization of the intermediate humulene (**6**, Scheme I) may take place at a single active site.[8,18] Further experiments to test this prediction and to establish the details of the pentalenene synthetase reaction are in progress.

Acknowledgment. The Bruker WM-250 NMR spectrometer used in this work was purchased with funds provided by the National Science Foundation and the Montedison Group of Milan. High-resolution mass spectra were obtained on a VG Micromass 7070H at the University of Pennsylvania. Strains of UC5319 were provided by Dr. L. J. Hanka of the Upjohn Co. We thank Professor Haruhisa Shirahama of Hokkaido University for providing us with a detailed experimental description of the synthesis of 2 reported in ref 5b.

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Models for the Photosynthetic Water Oxidizing Enzyme. 1. A Binuclear Manganese(III)-β-Cyclodextrin Complex

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Received September 15, 1982

The involvement of discrete binuclear and possibly tetranuclear clusters of Mn(III) and Mn(IV) in the enzyme that catalyzes the oxidation of water to oxygen in green plant photosynthesis[1] has prompted us to synthesis a binuclear Mn(III) model compound utilizing β-cyclodextrin (β-CD) as a ligand. β-CD is a naturally occurring cyclic oligomer containing seven glucose units.[2] The 7.0-Å internal diameter of the cavity of β-CD permits the formation of a large number of inclusion complexes.[3] This offers a method for modifying the redox properties and electron-transfer kinetics of coordinated metal sites. Although the Mn ligands in the enzyme have not been identified, they appear not to include thiol or thiolate[4] but may include nitrogen[1b] or oxygen donor ligands. α-CD and β-CD complexes with Cu(II) have been reported.[5] Stable coordination of Mn(III) and Mn(IV) by nonmacrocyclic polyhydroxy ligands such as sorbital and gluconate has been observed.[6]

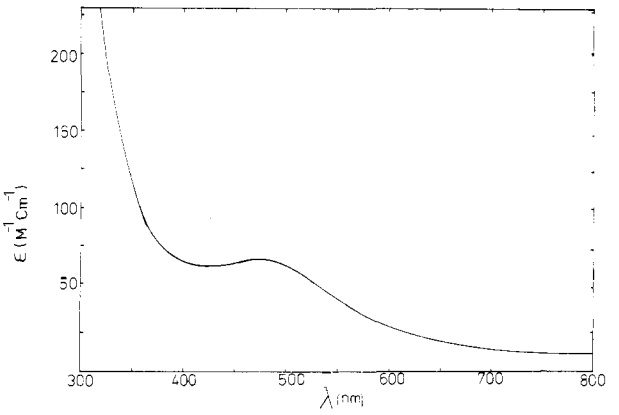

Figure 1. UV-visible spectrum of bis(μ-hydroxo)(β-cyclodextrin)dimanganese(III,III) in DMF.

Synthesis of Bis(μ-hydroxo)(β-cyclodextrin)dimanganese(III,III). β-CD (0.56 g, 0.5 mM) was dissolved in 30 mL of Ar-flushed DMF, Mn(II) acetate (0.26 g, 1.0 mM) was added, and the reaction mixture was stirred under Ar for 1 h. An alcoholic solution of NaOH (10 mL, 0.2 M) was added, and the resulting solution was exposed to bubbling air. After the solvent was stripped under vacuum, an excess of ethanol was added to precipitate the compound. It was filtered, washed with ethanol, and air-dried. The compound was recrystallized from 3:1 DMF-ethanol, yield 55%. An alternate procedure starting with Mn(III) acetate and the absence of oxygen also yielded the same compound, yield 20%. Mn was analyzed spectrophotometrically by oxidation to permanganate[7] and checked by EDTA titration of a reduced sample. These methods consistently gave 2.01 ± 0.04 Mn per β-CD·$2H_2O$ unit.

The compound is found to be soluble only in water, DMF, and Me_2SO. An aqueous solution of the compound is quite unstable and decomposes to hydrated oxides of Mn. However, in phosphate buffer (0.1 M, pH 9.2) the aqueous solution of the compound is comparatively more stable, observable precipitation occuring after 10-15 min. DMF and Me_2SO solutions of the compound are stable for days. The electronic spectrum of the compound in DMF exhibits a band at 482 nm, presumably due to an $^5E_g \rightarrow {}^5T_{2g}$-type transition typical of Mn(III)[8] (Figure 1). The oxidation state of Mn was confirmed to be 3+ by treating the compound with aqueous acid to remove the metal ion from the coordination sphere of cyclodextrin and reacting with Fe(II). No reaction is observed without prior release of Mn. The amount of Fe(III) generated was determined spectrophotometrically as the thiocyanate complex. One mole of the compound is found to react with 1.94 mol of Fe(II). Thus both of the Mn ions are in the trivalent state. The infrared spectrum shows the presence of all the prominent bands due to β-CD. A weakly enhanced infrared band is found in the complex at 652 cm^{-1}. This falls in the region for the $Mn_2(OH)_2$ stretching mode[9] and apparently excludes a μ-oxo bridge. ^1H NMR revealed that all the β-CD protons in the compound were not observable, even though the free ligand protons were easily identified. This shows broadening due to relaxation from the spin in the metal sites. Alternating current conductivity measurements in DMF showed an equivalent conductance of 8 mho cm^2 $equiv^{-1}$, indicating the compound to be essentially nonionic. A magnetic moment measurement by the Evans method gave a value of 3.51 μ_B per Mn at 302 K, which decreased to 3.38 μ_B at 224 K. This is well below the spin-only value (4.9 μ_B) for a mononuclear Mn(III) species, suggesting a possible weak antiferromagnetic

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