the carbon–carbon distance from that of graphite (case A) to that of benzene (case B) has very little effect on the calculated ionization potential (the difference is less than 1%) and only a moderate effect on the calculated optical transition energy. For both cases, the calculations predict that the lowest energy electronic transition should lie in the visible region of the spectrum; the absorption wavelength is found to be 492 nm for case A and 468 nm for case B.

Thus, the DV–Xα calculations predict that the lowest electronic transition in the soccerball-shaped cluster C_{60} should lie at an experimentally accessible energy. Measurement of this transition would provide valuable evidence as to whether or not the C_{60} species detected by Smalley and co-workers[1] is indeed shaped like a soccerball. The previous success of the DV–Xα method in the calculation of ionization potentials and optical excitations certainly suggests that its use as a predictive tool is warranted, and the results of experimental studies of the optical spectrum of C_{60} are eagerly awaited.

Acknowledgment. I thank Prof. George Schatz for suggesting this calculation, Prof. Mark Ratner for helpful discussions, and Prof. Don Ellis for the use of the DV–Xα program. Also, acknowledgment is made to an anonymous referee who suggested the possible importance of near-resonant ionization in enhancing the production of C_{60}^+ ions. This research was funded by the Chemistry Division of the National Science Foundation.

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Structure of Cervinomycin, a Novel Antianaerobic Antibiotic

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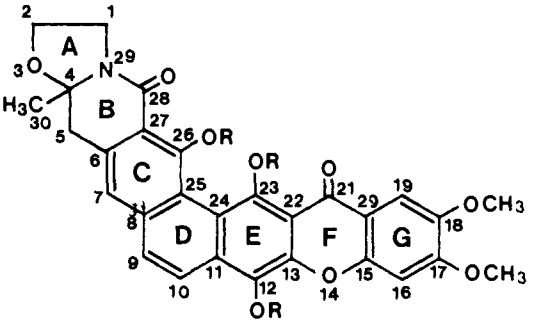
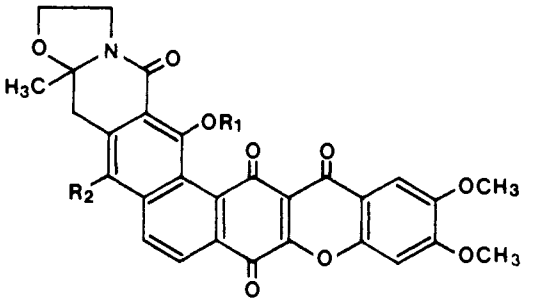
Cervinomycin[1] is an antianaerobic and antimycoplasmal antibiotic produced by *Streptomyces cervinus* sp. nov. The antibiotic consists of two components, A_1 (**1**), $C_{29}H_{23}NO_9$, and A_2 (**2**), $C_{29}H_{21}NO_9$, which are hardly soluble in any solvents. Triacetylcervinomycin A_1 (**3**) [mp 283–285 °C, $[\alpha]^{26}_D$ −115° (*c* 0.3, $CHCl_3$); EIMS, *m/z* 655 (M^+), $C_{35}H_{29}NO_{12}$], which was obtained in the course of the structure elucidation of cervinomycins, is developing as a medical drug because of its high solubility and low toxicity in addition to a potent antianaerobic activity against *Clostridium difficile*, *Reptococcus variabillis*, and *Streptococcus mutans*. In this paper we wish to report the structure of cervinomycin by means of 400-MHz NMR spectroscopy.

Methylation of **2** with CH_3I in the presence of Ag_2O in $CHCl_3$/MeOH afforded two methyl derivatives, *O*-methylcervinomycin A_2 (**4**) [mp >300 °C dec, $[\alpha]^{27}_D$ −499° (*c* 0.5, $CHCl_3$); EIMS, *m/z* 541 (M^+), $C_{30}H_{23}NO_9$; UV $\lambda_{max}^{CHCl_3}$ 248.0 nm (ϵ 42 700), 317.3 (27 300)] and *C,O*-dimethylcervinomycin A_2 (**5**) [mp >255 °C dec, $[\alpha]^{27}_D$ −459° (*c* 0.2, $CHCl_3$); EIMS, *m/z* 555 (M^+), $C_{31}H_{25}NO_9$; UV $\lambda_{max}^{CHCl_3}$ 252.2 nm (ϵ 35 000),



1 R = H
3 R = COCH$_3$



2 R_1, R_2 = H
4 R_1 = CH_3, R_2 = H
5 R_1 = CH_3, R_2 = CH_3
6 R_1 = $COCH_3$, R_2 = H

327.2 (21 500). The ^{13}C NMR spectrum (in $CDCl_3$) of **4** indicates the presence of a methyl (δ 23.3), two methylenes (δ 42.2 and 43.5), three methoxyls (δ 56.4, 56.7, and 63.2), an oxymethylene (δ 64.4), and a quaternary carbon (δ 92.1) bonded to an oxygen and a nitrogen atom. Compound **4** contains further 13 olefinic carbons in the region at 100–140 ppm, an amide group and five olefinic oxycarbons in 149–160 ppm, a doubly α,β-unsaturated carbonyl (δ 172.4), and two quinone carbonyls (δ 178.2 and 183.2). The location of two isolated olefinic protons (δ 7.13 and 7.64) was assigned from the structure of 3,4-dimethoxy-6-hydroxybenzoic acid, obtained by degradation of **2** (or **1**) with 0.5 N KOH in dioxane, which suggests the presence of partial structure (I) in cervinomycins.

For the connectivity of each functional group, a long-range ^1H and ^{13}C shift-correlated 2D NMR[2] and LSPD (^1H and ^{13}C long-range spin decoupling) experiment[3] were carried out for **4**. The existence of neighboring two methylene groups (C-1, δ 43.5; H-1a,1b δ 3.67 1 H m, 4.18 1 H m; C-2, δ 64.4 H-2a, 2b; δ 4.19 2 H t) placed between a nitrogen and an oxygen atom was confirmed from the proton coupling pattern. The observation of the ^1H and ^{13}C long-range couplings between H-1 and an amide carbon (C-28, δ 160.1) and between H-2 and a quarternary carbon (C-4, δ 92.1) indicated the existence of a five-membered ring including a nitrogen atom of an amide group and an oxygen atom. Long-range couplings were observed between a methyl proton (δ 1.43) and C-4 and between methylenic protons (H-5a,5b, δ 3.21, 3.29) and two sp^2 carbons (C-7, δ 121.3, and C-27, δ 118.5) and C-4. In the A, B type protons H-9 and H-10, appearing at δ 7.93 and 8.18, respectively, the former ($^3J_{CH}$ = 4.0 Hz) couples with C-7 and the later ($^3J_{CH}$ = 3.6 Hz), with C-12 (δ 178.2). These NMR evidences deduced the existence of a partial structure II consisting of conjugated five rings including a 1,4-benzoquinone moiety for **4**, as shown in Scheme I. The validity of structure II was also confirmed from the observation of the NOE effects

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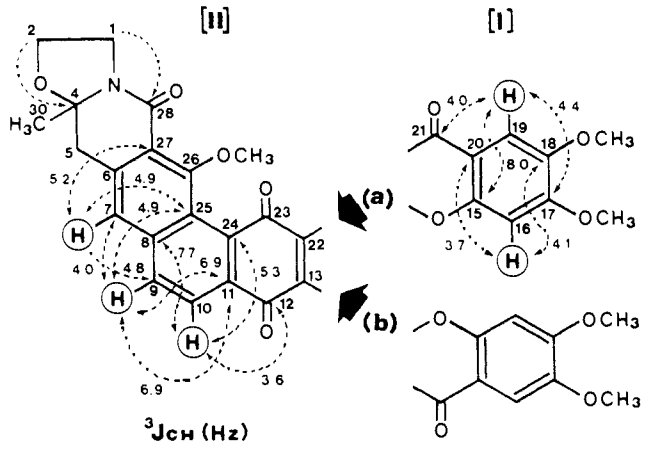
Scheme I



of H-7 in ring C with H-5 in ring B and H-9 in ring D. There are two possibilities, (a) and (b), for the connectivity of I to II as shown in Scheme I. In general, the chemical shift value of a quinone carbonyl carbon (or hydroquinone carbonyl) neighbor to the carbonyl of a γ-pyrone system[4] appears to be deshielded compared with the value when a quinone carbonyl locates to the ether oxygen of a γ-pyrone. The observation of $^4J_{CH}$ = 0.7Hz between H-10 and C-13 (δ 153.6) attached to an ether oxygen in addition to the above chemical shift values (C-12 δ 178.2; C-23, δ 183.2) afforded the validity of the connectivity a. The structures of **2** and **4** were also confirmed from the detailed NMR data of monoacetylcervinomycin A_2 (**6**): mp 283 °C, $[\alpha]^{27}_D$ −297° (*c* 0.32, $CHCl_3$); EIMS, *m/z* 569 (M^+), $C_{31}H_{23}NO_{16}$; UV $\lambda_{max}^{CHCl_3}$ 244 nm (ε 30950), 274 (21400), 307 (25500), 374 (9100), IR ($CHCl_3$): ν_{CO} 1775 cm^{-1}, which was obtained by acetylation of **2** in a similar manner of **3**. Thus, a polycyclic structure containing a xanthone skeleton was assigned for **2**.

The structure of the second methylation product **5** was assigned as the C-7 methylation product from a comparison with the chemical shift values of **4** and the observation of $^3J_{CH}$ of the methyl proton at C-7 with C-6 and C-8. It seems to be quite rare that the C-methylation occurs at the para position of a doubly α,β-substituted phenol derivative with CH_3I in the presence of Ag_2O. The hydroquinone structure of **1** was determined from the fact that acetylation of **1** with $(CH_3CO)_2O$ in pyridine in the presence of $(Et)_3N$ and oxidation of **1** with Ag_2O afforded a triacetate **3** and **2**, respectively.

Only three antibiotics of a xanthone structure have been reported in the literature, lysolipin I, a glycopeptide synthesis inhibitor,[5,6] albofungin (BA-180265, kanchanomycin), and chloroalbofungin, a DNA and RNA synthesis inhibitor.[7,8] As shown in ref 9, the xanthone ring of cervinomycin is identical with that of lysolipin I; however, it is a noteworthly that of albofungin is in an inverted arrangement. We are now investigating the biosynthetic correlation among cervinomycin, lysolipin I, and albofungin by feeding experiment using ^{13}C-labeled precursors.

Acknowledgment. We express our thanks to Hideki Shimizu of the Asahi Chemical Industries, Co., Ltd., for providing cervinomycins A_1 and A_2 samples.

Supplementary Material Available: Complete assignments of ^1H and ^{13}C chemical shifts in 400-MHz NMR are provided for compounds **2** and **4–6** (1 page). Ordering information is given on any current masthead page.

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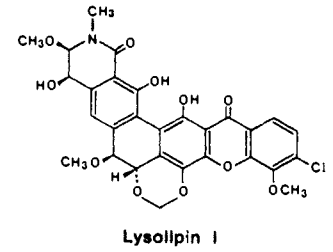
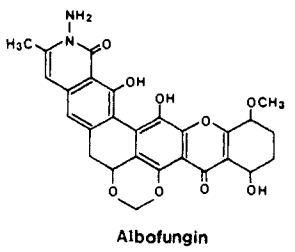

Lysolipin I


Albofungin

Synthesis and Characterization of the First Stable Cyanocyclophosphazenes

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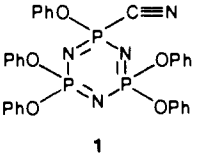
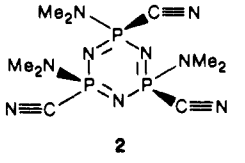
Cyclic and high polymeric phosphazenes are known that possess a wide variety of inorganic, organometallic, and organic side groups.[1-3] However, until now, no stable cyanophosphazenes have been reported, although attempts have been made to isolate such species.[4,5] Compounds of this type are of considerable interest as substrates for organic synthesis reactions based on the nitrile function, as ligands for transition metals, and as polymerization "monomers". We report here the synthesis and structure determination of the first stable cyanocyclophosphazenes.

Two typical cyanophosphazenes synthesized in this work are shown as **1** and **2**. Species **1** was prepared by the reaction of


1


2

monochloropentaphenoxycyclotriphosphazene, $N_3P_3Cl(OPh)_5$,[6] with potassium cyanide in acetonitrile at 82 °C during 24 h in the presence of tetra-*n*-butylammonium bromide as a phase-transfer agent. The yield was 81%. Anal. Calcd for $C_{31}H_{25}N_4O_5P_3$ (**1**): C, 59.42; H, 3.99;, N, 8.95. Found: C, 59.55; H, 4.24; N, 8.90. Low-resolution mass spectral analysis showed the expected molecular ion at *m/e* 626, and infrared analysis provided evidence for a cyano group stretch at 2200 cm^{-1}. Analysis of the ^{31}P NMR spectrum showed an A_2B spin system (δ_A 5.8, δ_B = −9.2, J_{PNP} = 55 Hz, relative to 85% H_3PO_4). Crystals of **1** were grown by the slow cooling of a warm, saturated solution in hexane, and the molecular structure was confirmed by single-crystal X-ray diffraction analysis. The structure of **1** is shown in Figure 1, and the important molecular dimensions are summarized in Table I.[7]

Species **2** was prepared by the reaction of *trans*-tris(dimethylamino)trichlorocyclotriphosphazene, $[NPCl(NMe_2)]_3$,[8] with potassium cyanide in acetonitrile in the presence of tetra-*n*-butylammonium bromide and traces (0.1%) of water at 82 °C during 10 days. The yield was 5%. Anal. Calcd for $C_9H_{18}N_9P_3$: C,

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(7) X-Ray analysis of **1**: space group $P2_1/n$; unit cell, *a* = 10.759 (4) Å, *b* = 9.662 (3) Å, *c* = 29.466 (4) Å, β = 96.92 (2)°; 5334 unique reflections measured on an Enraf-Nonius CAD4 diffractometer at 293 K; solved by direct and Fourier methods; full-matrix least-squares refinement; hydrogen atoms from difference map at fixed positions; final *R* = 0.045 and R_w = 0.047 for 3238 observed reflections with $I > 3\sigma(I)$.
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