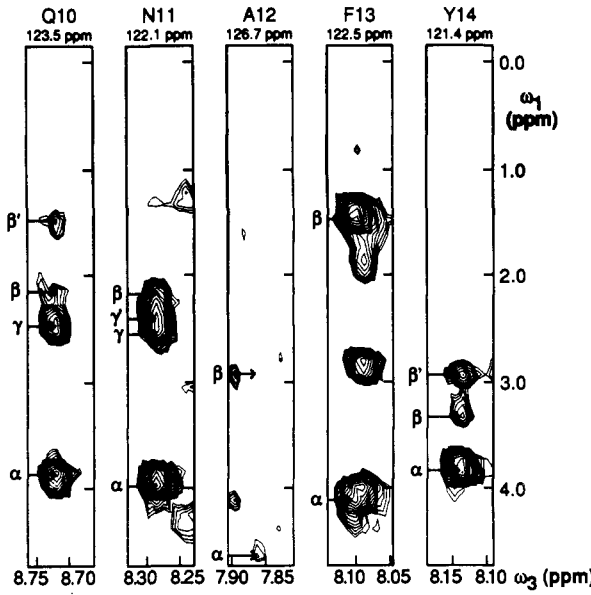

Figure 2. A panel showing strips from a 3D ^{15}N-edited HC(C)(CO)NH-TOCSY spectrum. These data were obtained using a 100% uniformly ^{13}C- and ^{15}N-enriched sample of a modified 8.2-kDa domain (called Z-Domain[9]) from the immunoglobulin-binding protein A of *Staphylococcus aureus* at a protein concentration of 2 mM in 10 mM K_2HPO_4, 0.2 mM NaN_3, pH 6.5, at a temperature of 30 °C. Shown in the figure are five representative $\omega_2 = {}^{15}N$ slices providing sequential connections for the polypeptide segment Gln-9–Tyr-14. Shown in each slice are 3D cross peaks between the side chain proton resonances of residue $i-1$ (ω_1 dimension), the ^{15}N resonance of residue i (ω_2 dimension), and the H^N resonance of residue i (ω_3 dimension). The slices themselves are labeled at the top with the ^{15}N chemical shift and the name of residue i. Each cross peak is labeled by an arrow with a tail at the ω_1 frequency of a side chain proton resonance of residue $i-1$ and a head at the ω_3 frequency of the backbone amide proton resonance of residue i. The sequential cross peak between $H^\alpha(11)$ and $H^N(12)$ was verified using a 2D version of the experiment recorded with a DIPSI-3 mixing time of 0 ms. This 3D data set was obtained using an isotropic mixing time of 24 ms and a total data collection time of ca. 40 spectrometer hours with a 500-MHz spectrometer. Data collection included 64 points in t_1 and t_2 and 1024 points in t_3, and the data were zero-filled prior to Fourier transformation, resulting in a final digital resolution of 66 Hz/point in ω_1, 18 Hz/point in ω_2, and 2.8 Hz/point in ω_3, respectively.

CSY pulse sequence is shown in Figure 1, and representative slices from a 3D spectrum recorded on an 8.2-kDa protein at 2 mM protein concentration are shown in Figure 2. A 2D spectrum exhibiting many connections between peripheral side chain protons and sequential backbone amide protons is presented in the supplementary material (Figure S1).

In HC(C)(CO)NH-TOCSY, the coherence transfer pathway depends on a series of one-bond scalar coupling constants that are all relatively independent of the protein conformation. Excellent 2D spectra for an 8.2-kDa protein were obtained using total collection times of 12–24 spectrometer hours on samples of 1–3 mM protein concentration on our 500-MHz NMR instrument. Cross peaks between Gly $C^\alpha H_{i-1}$ and $H^N{}_i$ resonances were observed to have phase shifts of 180° relative to other cross peaks in the spectra. Detailed analysis indicates that most of the cross peaks are sequential correlations from H^α, H^β, H^γ, H^δ resonances to the backbone ^{15}N and H^N resonances of the next amino acid in the sequence. For some asparagine and glutamine residues, cross peaks are also observed between aliphatic and side chain amide protons, uniquely identifying these spin systems. In fact, at appropriate isotropic mixing times the transfer from side chain aliphatic groups to these side chain amide protons is preferred over sequential magnetization transfer, attenuating sequential cross peaks in Asn-X or Gln-X dipeptide sequences. Aside from the cross peaks observed to these side chain amides, the carbonyl filter is highly selective for sequential connections and no intraresidue or long-range correlations involving backbone amide protons are observed.

The HC(C)(CO)NH-TOCSY pulse sequence of Figure 1 can be modified by introducing constant-time ^{13}C frequency labeling prior to the isotropic carbon-13 mixing period to generate 2D spectra which correlate peripheral side chain ^{13}C resonances with the backbone ^{15}N and H^N resonances of the next amino acid in the protein sequence. With this modification, the pulse sequence can also be run as a 4D-NMR experiment.

For small proteins HC(C)(CO)NH-TOCSY is quite efficient, is highly amenable to automated analysis by computer software, and provides significant advantages over conventional NOESY[2] or previously described triple-resonance[3-5] experiments for establishing sequential connections between spin systems of amino acid residues. By removing the coherence transfer step from $^{13}C^\alpha$ to $^{13}C'$ nuclei, the pulse sequence can also be modified into a related HC(C)NH-TOCSY experiment[10] which has intraresidue cross peaks from the side chain proton and carbon resonance of residue i to the backbone nitrogen and amide proton resonances of the same residue. Analyzed together, the HC(C)(CO)NH-TOCSY and the complementary HC(C)NH-TOCSY[10] experiments provide all of the information needed to determine sequence-specific resonance assignments of most backbone and side chain resonances in small proteins.

Acknowledgment. We thank Dr. B. Nilsson and Ms. L. Cedergren for providing the sample of ^{15}N,^{13}C-enriched Z-Domain. This work was supported by the National Science Foundation (DIR-9019313) and the National Institutes of Health (GM-47014).

Supplementary Material Available: Figure S1 depicting a 2D HC(C)(CO)NH-TOCSY spectrum using the pulse scheme outlined in Figure 1 (2 pages). Ordering information is given on any current masthead page.

(10) Lyons, B. A.; Montelione, G. T. *J. Magn. Reson.*, submitted for publication.

Total Synthesis of Westiellamide

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Received August 20, 1992

A considerable number of biologically active lipophilic cyclopeptides from marine organisms and fungi have been characterized in recent years.[1,2] Intensive structural and synthetic studies are addressing the use of naturally occurring and synthetic cyclic peptides in membrane transport and as models for hormone– and drug–receptor interactions.[3]

As a part of our program for the development of peptide mimetics, we have recently embarked on the total synthesis of westiellamide (**1**), a cyclic hexapeptide isolated by Moore et al.[4] from the terrestrial cyanophyte *Westiellopsis prolifica*. Westiellamide is identical to the earlier identified cycloxazoline[5]

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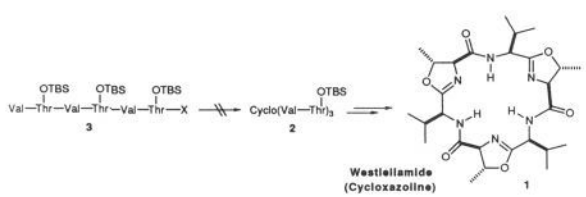
isolated from the marine ascidian *Lissoclinum bistratum* by Watters et al. It shows cytotoxic activity against MRC5CV1 fibroblasts, T24 bladder carcinoma, and KB and LoVo cell lines with an IC_{50} in the 0.5–2 μg/mL range. Due to their novel structural features and promising antineoplastic activities, oxazole- and thiazole-containing 18–24-membered cyclopeptides[6–11] are the focus of intensive synthetic and biological studies.[12,13] Westiellamide is one of the most toxic compounds among these natural products, and structure–activity studies of analogs of westiellamide are likely to shed more light on the molecular function of oxazolines[14] in cytotoxicity. In this communication, we report a highly efficient cyclotrimerization approach for the first total synthesis of westiellamide. Key features of our synthesis are (1) a novel direct interconversion of Thr and *a*Thr segments which allows the preparation of multigram quantities of peptides containing nonproteinogenic *allo*-threonine residues; (2) the use of turn-inducing oxazoline subunits to facilitate macrocyclic ring closure and inhibit diketopiperazine formation from activated dipeptides; and (3) the isolation of a novel 24-membered, highly symmetrical cyclooctapeptide analog of westiellamide.

Initially, we tried to use cyclo(Val-Thr)$_3$ (**2**) as a precursor to westiellamide. Whereas the preparation of the linear hexapeptide **3** by standard solution-phase peptide chemistry[15] proceeded uneventfully, attempted cyclization of **3** to **2** by phosphorazidate,[16] pentafluorophenyl ester,[17] Mukaiyama,[18] and other[19] methods failed to give any detectable amounts of cyclic products. The sequence of all β-branched L-amino acids in **3** appears to preclude a bent geometry suitable for cyclization.



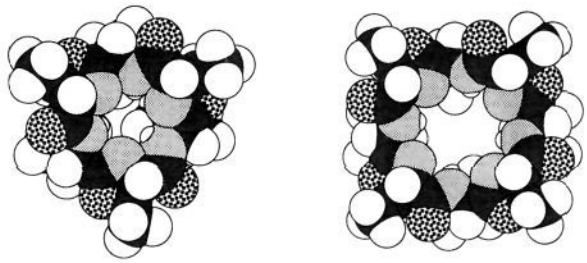
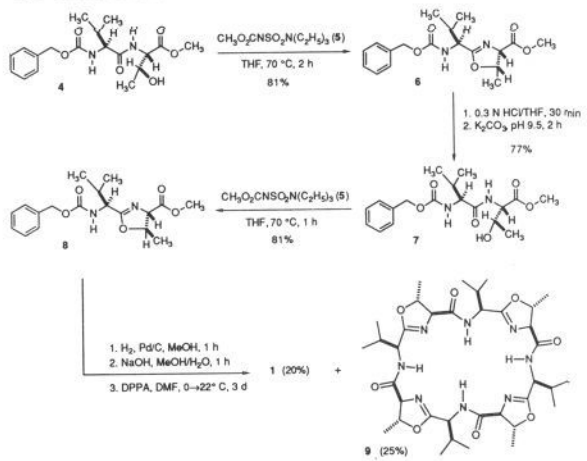


Figure 1. CPK models of westiellamide and cyclotetramer **9**.

Consequently, we turned our attention to conformationally preorganized precursors of westiellamide. Incorporation of an oxazoline subunit into a peptide sequence induces a reverse turn secondary structure.[20] Dipeptide oxazoline **6** was prepared in 81% yield by treatment of Cbz-Val-Thr-OMe (**4**) with the Burgess reagent (methyl *N*-((triethylammonio)sulfonyl)carbamate, **5**).[21] The intramolecular cyclization proceeded with inversion of the configuration at the threonine β-carbon. Room temperature acid hydrolysis of *cis*-oxazoline **6** resulted in an intermediate *O*-acyl amine,[22] which smoothly underwent an intramolecular *O*→*N*-acyl shift upon adjustment of the pH of the reaction mixture to 9.5 with K_2CO_3. Cbz-Val-*a*Thr-OMe (**7**) was isolated in >95% diastereomeric purity and 62% overall yield. Treatment of dipeptide **7** with reagent **5** led to the formation of the desired *trans*-oxazoline **8**.



Preparation of cyclic hexapeptides by cyclotrimerization of dipeptide sequences is usually prohibited by the rapid formation of diketopiperazines.[23] With oxazoline **8**, however, we expected no cyclization to diketopiperazine due to the rigid trans orientation of the modified amide bond fused into the five-membered ring.[24] Indeed, removal of the Cbz protective group by hydrogenolysis, followed by ester hydrolysis and treatment with 2 equiv of diphenyl phosphorazidate (DPPA) in DMF, led to the isolation of westiellamide in 20% yield and cyclotetramer **9** in 25% yield.[25] Incorporation of the oxazoline moiety into the dipeptide sequence both significantly facilitated the ring closure process via backbone bending and allowed the efficient cyclotrimerization approach

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toward the natural product by inhibiting diketopiperazine formation.

The ^1H NMR, ^{13}C NMR, and mass spectra of synthetic westiellamide ($[\alpha]^{21}_D$ = 130.0°, c = 0.1, MeOH)[26] were identical to those reported for the natural sample. With the exception of the valine β-H, which is shifted upfield, the ^1H NMR data for cyclotetramer **9** are very similar to those for trimer **1** and show that **9** has C_4 symmetry in the NMR time average at 22 °C in $CDCl_3$. The vicinal ^3J (NHCH) of 9.7 Hz in **9** corresponds to a HN$^{\alpha}$CH dihedral angle of 180° > θ > 160° with the valyl groups axial and the NH directed to the center of the molecule. Contrary to the related cyclooctapeptide ascidiacyclamide, which has two oxazoline and two thiazole subunits and adopts a rectangular form in solution and the solid state,[27] tetramer **9** is likely to adopt a novel square conformation with oxazolines located at each corner of the ring. This conformational preference is especially relevant for the formation of coordination complexes similar to expanded porphyrin[28] systems. The ease of formation of the 24-membered ring under the reaction conditions also suggests the possibility that **9** is a still unidentified product of *Westiellopsis* or *Lissoclinum* species. (See Figure 1.)

We are presently investigating further applications of oxazolines in cyclopeptide chemistry and the conformational and metal-chelating properties of westiellamide and macrocycle **9**, as well as further analog structures.

Acknowledgment. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Central Research Development Fund of the University of Pittsburgh. C.P.M. also acknowledges the DOE for a fellowship award.

Supplementary Material Available: Experimental synthetic procedures and data for **1**, **4**, and **6-9** (3 pages). Ordering information is given on any current masthead page.

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Cyclobutyne: The Ligand. The Synthesis and Molecular Structure of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2CH_2CH_2)(\mu\text{-}SPh)(\mu\text{-}H)$

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Although theoretical calculations have indicated that the molecule cyclobutyne, $C{\equiv}CCH_2CH_2$, lies on an energy minimum, there is as yet no conclusive experimental evidence for the existence of this molecule in the free state.[1] The ability of metal atoms to complex and stabilize highly reactive small molecules is well-known, and through complexation numerous species that would otherwise have been inaccessible have now been prepared and studied.[2] We now report that by using the stabilizing influence of three metal atoms we have been able to prepare and isolate the first example of a metal complex containing the ligand "cyclobutyne".

A cyclobutenyl grouping was introduced into a triosmium cluster complex by the reaction of $Os_3(CO)_{10}(NCMe)_2$[3] with 1-(phenylthio)cyclobutene,[4] $PhSC{=}CHCH_2CH_2$, at 25 °C. This yielded two products: $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}C{=}CHCH_2CH_2)(\mu\text{-}SPh)$, **1** (44%), and $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C{=}CHCH_2CH_2)(\mu\text{-}SPh)$, **2** (34%), by the addition of the 1-(phenylthio)cyclobutene and cleavage of the carbon-sulfur bond to the cyclobutenyl group.[5] The RS and cyclobutenyl groups are bridging ligands in both complexes. The molecular structures of **1** and **2** were established by single-crystal X-ray diffraction analyses, and an ORTEP drawing of the molecular structure of **2** is shown in Figure 1.[6] The η^2-cyclobutenyl ligand and a benzenethiolato ligand bridge the two metal atoms that are not mutually bonded in an open triosmium cluster. The formation of **1** involved in addition a degradation of the cluster to two metal atoms. Cleavage of RS substituents from unsaturated hydrocarbon groupings by triosmium clusters has been observed previously.[7]

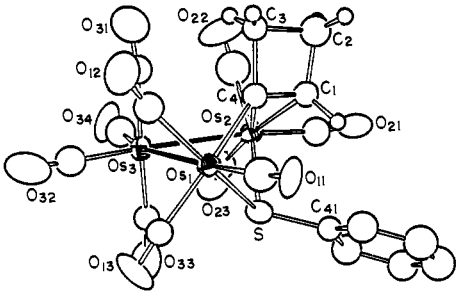

Figure 1. An ORTEP diagram of $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C{=}CHCH_2CH_2)(\mu\text{-}SPh)$, **2**. Selected interatomic distances (Å) for two independent molecules are Os(1)-Os(3) = 2.905 (2) [2.900 (2)], Os(2)-Os(3) = 2.938 (2) [2.958 (2)], Os(1)-C(4) = 2.06 (3) [2.16 (2)], Os(2)-C(4) = 2.39 (3) [2.40 (3)], Os(2)-C(1) = 2.53 (3) [2.41 (3)], and C(1)-C(4) = 1.38 (4) [1.29 (4)].

The transformation of the cyclobutenyl ligand into the cyclobutyne ligand was accomplished by treatment of compound **2** with Me_3NO in 25 mL of CH_2Cl_2 and heating to reflux for 30 h. Two products, **1** and the new complex $Os_3(CO)_9(\mu\text{-}SPh)$-

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(5) 1-(Phenylthio)cyclobutene (40 mg, 0.247 mmol) and 150 mg of $Os_3(CO)_{10}(NCMe)_2$ (0.161 mmol) were allowed to react in 25 mL of CH_2Cl_2 at 25 °C for 12 h. The products were separated by TLC using hexane solvent to yield 49.9 mg of yellow $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}C{=}CHCH_2CH_2)(\mu\text{-}SPh)$, **1** (46%), and 54.5 mg of yellow $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C{=}CHCH_2CH_2(\mu\text{-}SPh)$, **2** (34%). IR ($\nu_{CO}$ in hexane) for **1**: 2085 (m), 2056 (vs), 2009 (s), 1998 (s), 1982 (m). For **2**: 2102 (m), 2061 (vs), 2051 (m), 2018 (vs), 2013 (m), 2003 (w), 1994 (w), 1985 (w), 1975 (w). ^1H NMR for **2** (δ in $CDCl_3$): 7.187-7.358 (m, 5 H), 5.409 (s, 1 H), 3.098-3.125 (m, 2 H), 3.004-3.030 (m, 2 H).
(6) For details on the structure of **1**, see the supplementary material. For **2**: space group = $P2_1$, a = 13.638 (2) Å, b = 17.582 (4) Å, c = 9.946 (2) Å, β = 93.01 (2)°, Z = 4, 3264 reflections, R = 0.046. The crystal of **2** contains two symmetry independent molecules in the asymmetric crystal unit, but both molecules are structurally similar.
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(8) **2** (62 mg, 0.0612 mmol) and 4.5 mg of Me_3NO (0.0612 mmol) in 25 mL of CH_2Cl_2 were heated to reflux for 30 h. The products were separated by TLC in hexane to yield 9.8 mg of yellow **1** (21%) and 23 mg of greenish yellow $Os_3(CO)_9(\mu\text{-}SPh)(\mu_3\text{-}\eta^2\text{-}C{=}CCH_2CH_2)(\mu\text{-}H)$, **3** (35%). IR ($\nu_{CO}$ in hexane) for **3**: 2103 (w), 2079 (vs), 2053 (s), 2031 (m), 2018 (m), 2013 (s), 1994 (w), 1979 (w). Anal. Calcd for **3** (found): C, 23.17 (22.97); H, 1.02 (0.99). ^1H NMR at 27 °C (in $CDCl_3$): -17.41 (1 H, s), 4.34 (2 H, d, ^2J = 10 Hz), 3.66 (2 H, d, ^2J = 10.5 Hz), 7.35 (1 H, Ph, s), 7.25-7.13 (4 H, Ph, m). At -73 °C (in CD_2Cl_2): -17.60 (1 H, s), 3.50 (1 H, m), 3.67 (1 H, m), 4.20 (1 H, m), 4.36 (1 H, m), 7.12 (2 H, m), 7.20 (2 H, m), 7.33 (1 H, s). $^{13}C\{^1H\}$ NMR at -68 °C (in CD_2Cl_2): CH_2, 50.5, 51.0; Ph, 128.5, 128.9, 132.1, 140.0; CO, 168.5, 169.8, 171.8, 172.2, 175.5, 176.0, 177.7, 178.9, 181.6; $\equiv C$, 156.9, $\equiv C$, 193.9 ppm. $^{13}C\{^1H\}$ NMR at 25 °C (in $CDCl_3$): Ph, 142.0, 131.9, 128.9, 128.5; CH_2, 50.6 ppm.
(9) Crystal data for **3**: space group = $P2_1/n$, a = 10.954 (2) Å, b = 16.540 (3) Å, c = 12.495 (2) Å, β = 91.98 (2)°, Z = 4, 2233 reflections, R = 0.033.

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