Table I. The Sequence-Specific Chemical Shift Assignments for Leu-Arg-Arg-Cys↔Cys-Leu-Gly

residue	NH	C_α	C_β	other
Leu1	8.22	3.85	1.58, 1.60	CH_3, 0.97, 0.91; C_γ, 1.23
Arg2	8.85	4.43	1.68, 1.78	C_γ, 1.58, 1.61; C_δ, 3.17; NH_η, 7.50; NH_ϵ, 8.04
Arg3	8.41 (c), 8.54 (t)	4.32	1.63, 1.74	C_γ, 1.56; C_δ, 3.12; NH_η, 7.52; NH_ϵ, 8.27
Cys4	8.00 (c), 8.02 (t)	4.84 (c), 4.86 (t)	2.81, 3.38 (c); 3.26, 3.74 (t)	
Cys5	8.04 (c), 8.18 (t)	4.92 (c), 4.86 (t)	2.81, 2.98	
Leu6	8.63 (c), 7.91 (t)	4.37 (c), 4.33 (t)	1.58, 1.71	CH_3, 0.95, 0.97; C_γ, 1.24
Gly7	8.23	3.72, 2.72		

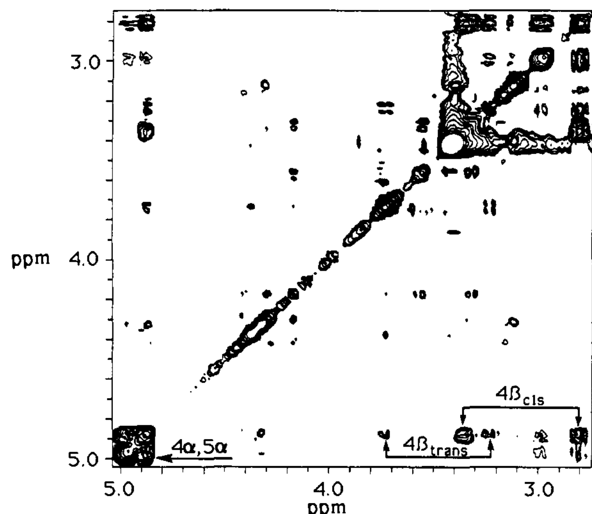
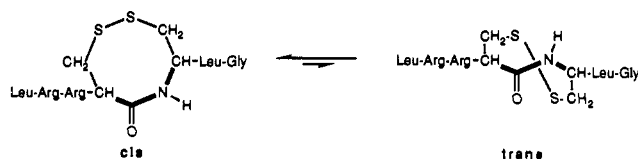


Figure 1. An expansion of the aliphatic region of the two-dimensional NOESY spectrum of Leu·Arg-Arg-Cys⇔Cys-Leu-Gly (2.5 mM in 100% DMSO-d_6). Conducted at 400 MHz on a Varian-400S spectrometer at 25 °C. The pure phase absorption NOESY spectrum was recorded by using the hypercomplex method[15] at 400-ms mixing time.

We prepared[12] the heptapeptide Leu-Arg-Arg-Cys-Cys-Leu-Gly (**1**)[13] and oxidized this species to the corresponding intramolecular disulfide (**2**) by Snyder's protocol.[14] Amino acid analysis and FAB mass spectroscopy of **2** proved to be consistent with the desired structure. Two-dimensional correlated (COSY) and nuclear Overhauser enhancement (NOESY) spectroscopies provided the sequence-specific chemical shift assignments (Table I). An expansion of the aliphatic region of the NOESY spectrum is provided in Figure 1. A strong Cys-4 $C^\alpha H \rightarrow$ Cys-5 $C^\alpha H$ NOE is evident just off the diagonal. In addition, we also observed a through-space interaction between the Cys-4 NH and the Cys-5 $C^\alpha H$. Both sets of NOEs are diagnostic of a cis peptidic linkage.[16]

Two sets of resonances are present for the Cys⇔Cys dyad as well as for the residues immediately adjacent (i.e., Arg-3 and Leu-6) to the dyad. This is a consequence of the presence of both the cis and trans isomeric forms, with the former accounting for 70 ± 5% of the total population. In contrast, Chandrasekaran had previously concluded that it is not possible for the peptide bond in a Cys↔Cys dyad to occupy the trans configuration.[17]



(12) Peptide synthesis performed as previously described in the following: Prorok, M.; Lawrence, D. S. *J. Biochem. Biophys. Methods* **1989**, *18*, 167-176.
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In summary, we have found that the peptidic linkage joining the two cysteine residues in Leu-Arg-Arg-Cys⇔Cys-Leu-Gly exists predominantly in the cis isomeric form. Since the Cys⇔Cys dyad is easy to prepare, such a molecular constraint should prove to be of general utility in conferring a configurational bias on otherwise conformationally flexible peptides. In addition, recent efforts in de novo protein design have served to generate interest in the construction of secondary structural elements, both artificial and peptidic.[18] The Cys⇔Cys dyad offers the potential of incorporating bends or turns into natural and unnatural proteins via insertion of the unoxidized precursor by the standard protocols of either solid-phase peptide synthesis or the recombinant DNA methodology.[19]

Acknowledgment. We are pleased to acknowledge the generous financial support of the American Cancer Society (BC-664).

(17) (a) Chandrasekharan, R. *Proc. Indian Acad. Sci., Sect. A* **1968**, *68*, 13. The crystal structures of Cys⇔Cys and Boc-Cys⇔Cys-OMe have been reported by Capasso et al. and Hata et al., respectively. (b) Capasso, S.; Mattia, C.; Mazzarella, L. *Acta Crystallogr.* **1977**, *B33*, 2080. (c) Hata, Y.; Matsuura, Y.; Tanaka, N.; Ashida, T.; Kakudo, M. *Acta Crystallogr.* **1977**, *B33*, 3561. In both cases, the peptide bond assumed only the cis configuration. It is possible that the trans isomer, if present, was lost during the crystallization process.
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(19) A complete analysis of the secondary structural elements associated with **2**, along with molecular modeling studies, will be presented elsewhere.

Structures of the Efrapeptins: Potent Inhibitors of Mitochondrial ATPase from the Fungus *Tolypocladium niveum*

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The efrapeptins are a series of novel peptides produced by the entomopathogenic fungus *Tolypocladium niveum*.[1] In addition to their insect toxicity, they strongly inhibit mitochrondrial ATPase and photophosphorylation in chloroplasts.[1] The efrapeptins probably act by binding competitively to the catalytic site of the soluble (F_1) part of mitochondrial ATPase and blocking an essential arginine residue at the adenine nucleotide binding site.[2]

(1) For leading references, see: (a) Lucero, H.; Lescano, W. I. M.; Vallejos, R. H. *Arch. Biochem. Biophys.* **1978**, *186*, 9. (b) Kohlbrenner, W. E.; Cross, R. L. *Arch. Biochem. Biophys.* **1979**, *198*, 598 and references therein.
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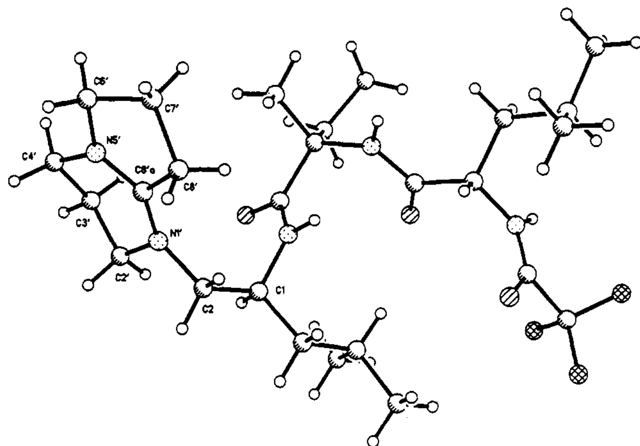
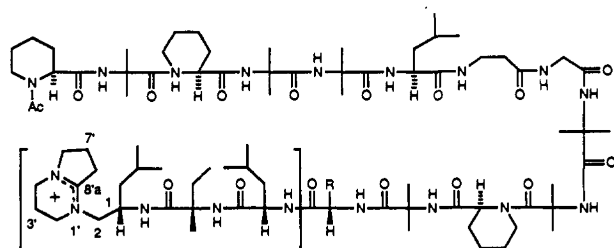


Figure 1. A computer-generated perspective drawing of hydrolytic fragment derivative **4**. The absolute configuration was set by the L-leucine, and the trifluoroacetate anion has been omitted for clarity.

While the efrapeptins have been exploited for their interesting biological properties,[3] their structures have not been elucidated. In a noteworthy contribution,[4] Bullough et al. proposed an amino acid sequence for efrapeptin D. Their proposed structure, Ac-L-Pip-Aib-L-Pip-Aib-Aib-L-Leu-β-Ala-Gly-Aib-Aib-L-Pip-Aib-Gly-L-Leu-L-Iva-Aib-X, while wrong in detail, points out several interesting features of the hydrophobic efrapeptins: a large number of aminoisobutyric acid (Aib) and pipecolic acid (Pip) residues, the unusual amino acids β-alanine and L-isovaline (Iva), and most importantly, the presence of a novel but uncharacterized carboxyl terminal group (X). As part of our work on fungal insect toxins, we reisolated the efrapeptins and in this communication report the complete stereostructures of efrapeptins D and F as **1** and **2**, respectively.



1 R = H (Ac-L-Pip-Aib-L-Pip-Aib-Aib-L-Leu-β-Ala-Gly-Aib-Aib-L-Pip-Aib-Gly-L-Leu-L-Iva-X)
2 R = CH_3 (Ac-L-Pip-Aib-L-Pip-Aib-Aib-L-Leu-β-Ala-Gly-Aib-Aib-L-Pip-Aib-L-Ala-L-Leu-L-Iva-X)

An extract of *T. niveum*[5] was fractionated[6] using an insect toxicity bioassay[7] to yield two major and three minor efrapeptins. The amino acid sequences of the two major efrapeptins, D and F, were established by amino acid analysis, FABMS fragmentation pattern, and GC–MS (EI and CI) analysis of volatile derivatives of partial hydrolysates.[8] All of the chiral amino acids were shown to have the *S* (L) absolute configuration by chiral GC and other analyses.[9] Efrapeptin D (**1**) differed from efrapeptin F (**2**) by one Gly/Ala replacement.

We first attempted to elucidate the structure of the C-terminal blocking group by examining hydrolytic fragments. Hydrolysis (6 N HCl, 110 °C, 12 h) afforded a fragment[10] that was identified by FABMS at H-L-Leu-L-Iva-X (**3**, see square brackets in **1**). High-resolution FABMS gave an M^+ at 436.3647 ($C_{24}H_{46}N_5O_2$, calcd 436.3652) suggesting five degrees of unsaturation in a *cationic* parent molecule. The nature of the C-terminal group was elucidated by a single-crystal X-ray diffraction analysis of **4**, the trifluoroacetate salt of the trifluoroacetyl derivative[11] of hydrolytic fragment **3**. Compound **4** crystallized in the monoclinic space group $P2_1$ with a = 11.101 (3) Å, b = 14.844 (2) Å, c = 11.660 (2) Å, and β = 116.23 (1)° with an asymmetric unit of $C_{28}H_{45}N_5O_5F_6$. Diffraction data were collected with θ–2θ scans on all unique reflections with $2\theta \leq 115°$, and after correction for Lorentz, polarization and background effects, 2292 (93%) were judged observed ($|F_o| \geq 4\sigma(|F_o|)$). Refinement of the X-ray structure was complicated by the disorder of the trifluoroacetate groups, but the current crystallographic residual is 6.9% for the observed data. A computer-generated perspective drawing of the final X-ray model is given in Figure 1.

Spectral measurements of **1–3** were completely in accord with the X-ray structure. For example, a fragment ion in the HRFABMS at 138.116 ($C_8H_{14}N_2$, calcd 138.1157) represents cleavage of the terminal bicyclic fragment between C1 and C2, and a prominent fragment ion at m/z 138 was observed in the FABMS of peptides **1–4**. A peak in the ^{13}C NMR spectrum at 166.1 ppm, assigned to the C8′a, was observed in the spectra of **2** and **3**. The ^1H NMR spectrum (COSY, *J*-resolved, RELAYH) showed two $CH_2CH_2CH_2$ fragments. In one, the CH_2 at δ 2.15 (7′) showed connectivity to two pairs of CH_2 multiplets at 3.73 and 3.81 (6′) and 3.03 and 3.18 (8′). In the other, the CH_2 multiplet at 2.06 (3′) was connected to 3.43 and 3.64 (2′) and 3.41 (4′, superimposed on other peaks). The biosynthesis of the C-terminal blocking group is unclear, but formally represents the alkylation product of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) with L-leucinol, a surprising reaction of two well-known molecules.[12]

Efrapeptins D (**1**) and F (**2**) were toxic to *Leptinotarsa decemlineata* (LC_{50}'s of 18.9 and 8.4 ppm, respectively) and inhibited the mitochondrial ATPase from fungi (*Metarhizium anisopliae* and *T. niveum*) and insects (*Musca domestica*).[13] The activity of the efrapeptins primarily resides in the C-terminus since one of the hydrolytic fragments, Ac-Aib-Gly-L-Leu-L-Iva-X, showed a dose response inhibition of *M. domestica* ATPase albeit with a lower specific activity than that of the full peptide.

Acknowledgment. We thank the USDA-ARS Plant Protection Research Unit at Cornell University for supplying the fungal isolate; Anne Macaulay and Nancy Underwood for technical assistance; the Middle Atlantic Spectrometry Laboratory (Baltimore, MD), a NSF Shared Instrumentation Facility; Dr. A. J. Alexander of the Mass Spectrometry Facility at Cornell University for help in interpreting the mass spectra; and Dr. Aidan Harrison and David J. Fuller of Cornell's NMR Facility for help with the

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(4) Bullough, D. A.; Jackson, C. G.; Henderson, P. J. F.; Cottee, F. H.; Beechey, R. B.; Linnett, P. E. *Biochem. Int.* **1982**, *4*, 543.

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(6) The CH_2Cl_2 soluble broth extract was flash chromatographed on SiO_2, and the active fraction was purified by chromatography over Sephadex LH-20 followed by preparative TLC on SiO_2 (R_f, 0.5, 0.45; toluene/2-butanone/EtOAc/HCO_2H/H_2O, 3:12:25:5:5). Final purification was achieved by HPLC with RPC_8. **1**: $[\alpha]^{22}_D$ −3.1° (c 0.32, $CHCl_3$); λ_{max} (MeOH) 208, 230 (sh) nm. **2**: $[\alpha]^{22}_D$ −5° (c 0.4, $CHCl_3$); λ_{max} (MeOH) 208, 230 (sh) nm. The identities of **1** as efrapeptin D and **2** as efrapeptin F are based on comparison with the chromatographic properties given in ref 4.

(7) Insect toxicity bioassays were performed on *L. decemlineata* (Coleoptera) in a foliar spray assay.

(8) The peptide mixture was hydrolyzed with concentrated HCl (37 °C, 12 h). Nau, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 75. Konig, W. A.; Aydin, M. *Chem. Pept. Proteins* **1982**, *1*, 173.

(9) The Ala and Leu absolute configurations were determined by GC analysis of the *N*-TFA, OMe ester of peptide hydrolysate on a chiral column (*N*-*n*-lauroyl-*N*-L-valine-*tert*-butylamide). The absolute configuration of Pip was established by isolation and measurement of the optical rotation. The absolute configuration of Iva was established by the X-ray analysis.

(10) Sephadex-purified toxin was hydrolyzed and chromatographed on cellulose followed by HPLC using RPC_4 to furnish **3**.

(11) Compound **3** was treated with trifluoroacetic anhydride and subjected to HPLC to furnish **4**.

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NMR experiments. Funding was partially provided by E. I. du Pont de Nemours, USA, and the NIH (CA24487) (J.C.).

Supplementary Material Available: FAB mass spectra of **1** and **2**, NMR spectra (^{1}H, ^{13}C, and COSY) of **3**, and crystallographic information on **4** (10 pages). Ordering information is given on any current masthead page.

Mechanism for the Photocyclization of *o*-Alkyl Ketones to Cyclobutenols

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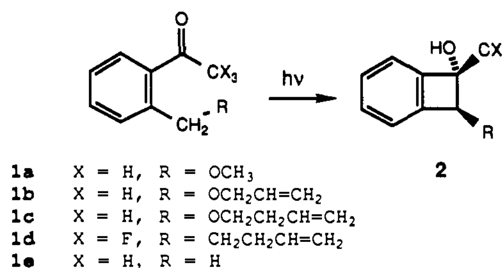
One of the unsolved puzzles of organic photochemistry has been the efficient formation of benzocyclobutenols from 2,6-dialkylphenyl ketones but not from simple *o*-alkylphenyl ketones.[1] It has been commonly assumed that *o*-alkyl ketones form only enols, which revert to ketone or can be trapped by various dienophiles,[1] although a couple of compounds were reported to provide benzocyclobutenols in low yield.[2,3] We report that a variety of *o*-alkyl ketones do in fact form cyclobutenols efficiently, quantitatively, and often stereoselectively and that the mechanism involves thermal electrocyclic closure of the initial dienol photoproducts.

Scheme I depicts several acetophenones that we have found to yield benzocyclobutenols as the major or only photoproducts upon irradiation of dilute ketone with wavelengths >290 nm.[4] In all cases a single diastereomer was produced.[5] NOE analysis of cyclobutenol **2a** indicated the *E* stereochemistry,[6] as did the concentration dependence of the OH signals in both IR and NMR spectra. (The *Z* isomers presumably would be internally hydrogen bonded.) Heating the alcohols at 80 °C or higher converts them quantitatively to the starting ketones, as has been observed for a wide variety of benzocyclobutenols.[3,7-9] This observation confirms Wilson's suggestion that dienol formation probably had been overlooked in the past because gas chromatographic analysis would thermally open the cyclobutenols.[3] It also confirms the *E* stereochemistry of **2a**, since the *Z* isomer would not open thermally at low temperatures.[7]

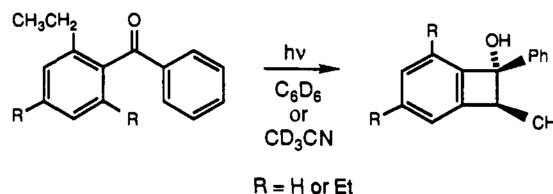
We have also studied several benzophenones. *o*-Methylbenzophenone forms cyclobutenol with no evidence for the other

Scheme I



1a X = H, R = OCH_3
1b X = H, R = $OCH_2CH{=}CH_2$
1c X = H, R = $OCH_2CH_2CH{=}CH_2$
1d X = F, R = $CH_2CH_2CH{=}CH_2$
1e X = H, R = H

products reported by Wilson.[3] *o*-Ethylbenzophenone forms the (*E*)-cyclobutenol quantitatively with no trace of the *Z* isomer in a quantum yield estimated as 0.5.[10] The same single isomer was obtained in acetonitrile solvent. In CD_3OD used as received, no photoproduct was observed by NMR, but efficient benzylic H–D exchange[11,12] took place as evidenced by disappearance of the methylene quartet and collapse of the methyl triplet to a broad singlet with unresolved deuterium coupling. Adding methanol to solutions containing benzocyclobutenol caused no change, so this NMR solvent prevented formation of cyclobutenol. 2,4,6-Triethylbenzophenone also gives only the (*E*)-cyclobutenol in benzene, acetonitrile, and methanol-d_4.



Early workers disagreed over whether dienol is formed from cyclobutenol[1] or cyclobutenol from dienol.[13] The former seems unlikely, since it is hard to imagine why a triplet biradical, known to be the first product in these reactions,[14,15] would directly cyclize only to the less stable cyclobutenol. Nonetheless, we sought firmer evidence. If cyclobutenols were formed before the dienols, irradiation of ketones in the presence of additives that react with the dienols would not quench cyclobutenol formation. However, benzene-d_6 solutions containing **1a**, *o*-ethylbenzophenone, or 2,4,6-trimethylbenzophenone and one crystal of *p*-toluenesulfonic acid (~0.005 M) produce *no* benzocyclobutenol after hours of irradiation. Valerophenone in benzene containing acid reacts completely after 15-min irradiation; so added acid does not destroy the ketones' intrinsic photoreactivity.[16] Addition of the same amount of acid to solutions containing only benzocyclobutenol causes very slow *E*/*Z* interconversion[17] with only trace reversion to ketone. (After several days the *Z*:*E* ratio stabilized at 7:3.) Since the cyclobutenols are stable to acid while the dienols are rapidly converted to ketone by acid, we conclude that *all* cyclobutenol formation must occur from the first-formed dienols.

It is well-known that both *E* and *Z* enols are formed from the triplet ketones.[14,15] The latter undergo a very rapid 1,5-sigmatropic H shift to regenerate ketone,[16] while the former live for as long

(1) Sammes, P. G. *Tetrahedron* **1976**, *32*, 405.
(2) Arnold, B. J.; Mellows, S. M.; Sammes, P. G.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 401.
(3) Wilson, R. M.; Hannemann, K. *J. Am. Chem. Soc.* **1987**, *109*, 4741.
(4) Acetonitrile solutions (450 mL) 0.02 M in ketone were irradiated with a Pyrex-filtered 450-W Hanovia mercury arc. Products were isolated by silica gel chromatography with 5% ethyl acetate in petroleum ether eluent. At 75% conversion, yields were quantitative. For **1d**, 3-h irradiation was sufficient; the other ketones required 20 h.
(5) For **2a**: mp 73 °C; ^{1}H NMR ($CDCl_3$) δ 1.62 (s, 3 H), 3.20 (br s, 1 H, D_2O exchanged), 3.56 (s, 3 H), 4.70 (s, 1 H), 7.25–7.38 (m, 4 H). For **2b**: IR (CCl_4) 3560, 3400, 3050, 1620, 790 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.61 (s, 3 H), 3.20 (br s, 1 H, OH), 4.18–4.33 (qdt, *J* = 13, 5.7, 1.6 Hz, 2 H), 4.84 (s, 1 H), 5.21–5.62 (m, 2 H), 5.93–6.08 (m, 1 H), 7.25–7.35 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 23.76, 71.16, 80.27, 85.05, 117.87, 121.82, 126.5, 129.66, 130.26, 136.51, 142.69, 151.96.
(6) For **2a**, irradiation at 4.70 ppm (methine proton) produced a much larger NOE enhancement of the methoxy proton resonance than of the methyl resonance.
(7) Arnold, B. J.; Sammes, P. G.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 409, 415.
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(17) The more stabe *Z* isomer is characterized by a 0.40 ppm higher chemical shift for the methyl group than in the *E* isomer. For a summary of previous such observations, see: Wagner, P. J.; Meador, M. A.; Park, B.-S. *J. Am. Chem. Soc.* **1990**, *112*, 5199.

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