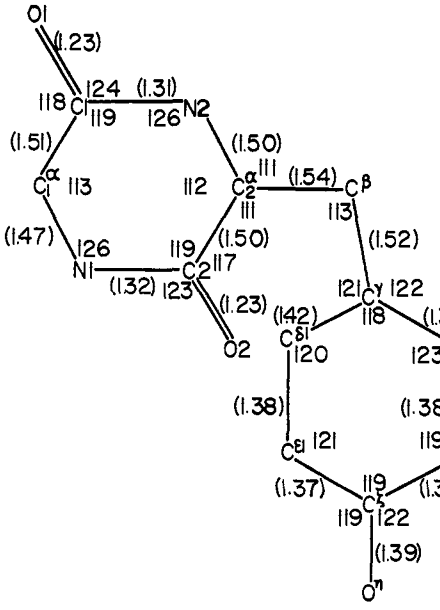

Figure 1. Bond angles and bond distances[10] in *cyclo*-glycyl-L-tyrosyl. Bond distances are shown in parentheses.

boat conformations, one with the benzyl substituent quasiaxial ("flagpole," Figure 2B), and the other with this substituent quasiequatorial ("bowsprit," Figure 2C).[5] We find *c*-Gly-L-Tyr to be buckled to the extent of 10–20° toward the boat conformation (B); the relevant torsional angles are $\phi_1 = 19°$, $\psi_1 = -13°$, $\phi_2 = 16°$, $\psi_2 = -10°$. The ϕ and ψ values are 10–13° smaller and of opposite sign to the corresponding angles in *c*-L-Ala-L-Ala, which is buckled in the opposite direction, with the methyl groups quasiequatorial (Figure 2C).[4,9] The amide groups deviate only slightly from planarity ($\omega_1 = -4°$, $\omega_2 = -7°$) so that there is little "twist" in the boat.

The χ^1 (C^α, C^β) angle is 55° so that the aromatic ring lies directly over the DKP ring (Figure 2B) in agreement with nmr studies in solution which have shown that arylmethyl side chains prefer this folded conformation[2,3,5] (the F rotamer).[3] The 71° $\chi^{2,1}$ angle tilts the aromatic ring plane 19° away from the symmetrical position perpendicular to the $C^\alpha C^\beta C^\gamma$ plane. Pullman and coworkers have assumed a planar DKP ring in molecular orbital calculations on *c*-Gly-L-Phe and found $\chi^1 = 60°$, $\chi^2 = 60°$ for the most stable conformation.[8] Empirical potential energy calculations employing a planar DKP ring give $\chi^1 = 60°$, $\chi^2 = 90°$.[16]

An overall picture of the effect of substituents on the conformation of the DKP ring is beginning to emerge from nmr and X-ray data. Application of a recently developed expression relating the peptide NH-C^αH coupling constant to dihedral angle[17] indicates that, in dimethyl sulfoxide solution, a number of monosubstituted diketopiperazines, including *c*-Gly-L-Tyr, *c*-Gly-L-Phe, *c*-Gly-L-Trp, and *c*-Gly-L-Val, prefer a boat conformation with the substituent in a flagpole type of orientation (Figure 2B).[3,18] This conformation was proposed earlier for *c*-Gly-L-Phe and *c*-D-Ala-L-Phe in trifluoroacetic acid on the basis of aromatic ring shielding effects in the nmr spectra.[5] Figure 2 shows that, for the folded conformation, interaction between the substituent and the DKP ring is greatest for the flagpole orientation (Figure 2B). When the second amino acid has the L configuration as in Figure 2, both substituents may not be able to assume the flagpole orientation, particularly when one substituent is aromatic. Models show that planarity can remove the side-chain interference and still maintain some interaction between a substituent and the DKP ring. The dominance of the planar conformation for *c*-L-Ala-L-Phe has been explained on this basis;[5] *c*-L-Val-L-Tyr also favors the planar conformation found in diketopiperazine itself, *c*-Gly-Gly.[3,18]

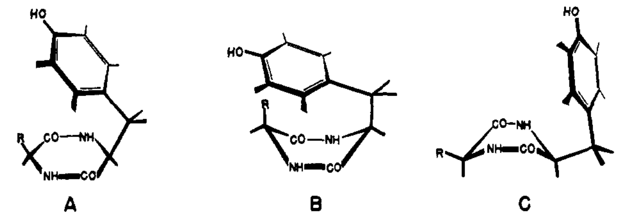

Figure 2. The folded form ($\chi^1 = 60°$) of a tyrosyl residue in cyclic dipeptides with planar and boat conformations of the diketopiperazine ring.

In the absence of aromatic side chains, the lessened importance of intramolecular interactions apparently makes the various DKP ring conformations quite close in energy and makes other effects such as crystal packing forces more important. Thus, one would expect the DKP ring to minimize ring strain by taking whichever boat conformation avoids side chain interference, but in the crystalline state, both planarity[10,15,19] and the bowsprit boat conformation (Figure 2C) have been found.[4,9]

The DKP ring conformation, then, appears to be primarily determined by the maximization of DKP aromatic ring interaction and the avoidance of side-chain interference. Strain in the DKP ring system enters to a lesser extent. The solution of the *c*-L-Ser-L-Tyr crystal structure, now in progress, should allow further evaluation of these effects.

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(16) (a) G. N. Ramachandran, University of Chicago, personal communication, 1971; (b) compare A. V. Lakshminarayanan, V. Sasisekharan, and G. N. Ramachandran in ref 7, p 61.

(17) G. N. Ramachandran, R. Chandrasekaran, and K. D. Kopple, *Biopolymers*, in press.

(18) K. D. Kopple, Illinois Institute of Technology, personal communication, 1971.

(19) R. B. Corey, *J. Amer. Chem. Soc.*, **60**, 1598 (1938).

Lawrence E. Webb,* Chi-Fan Lin
Department of Chemistry, Illinois Institute of Technology
Chicago, Illinois 60616
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Photooxidation of Aqueous Benzene.
I. Identification of the Product as 1,3-Cyclopentadiene-1-carboxaldehyde[1]

Sir:

Irradiation of benzene at 253.7 nm in aerated water at pH 4–8 has been reported[2] to yield an acidic aldehyde, tentatively identified as 4*H*-pyran-2-carboxaldehyde. A recent communication[3] supporting this assignment

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) E. Farenhorst, *Tetrahedron Lett.*, 4835 (1968).

(3) M. Luria and G. Stein, *Chem. Commun.*, 1650 (1970).

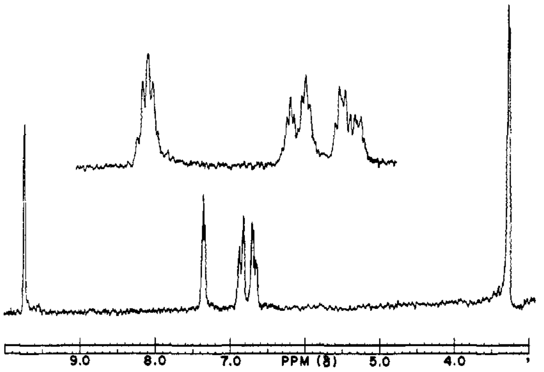


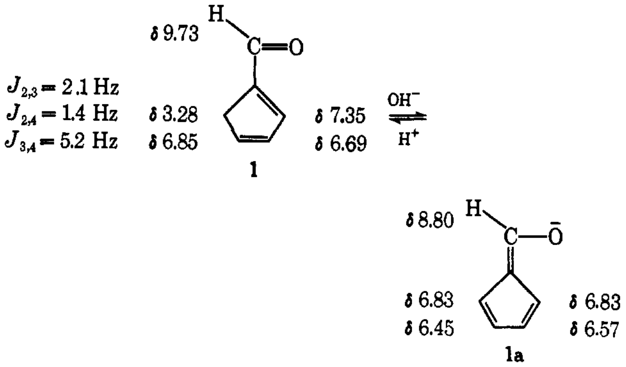
Figure 1. Spectrum (CCl_4, TMS, −20°, 100 MHz) of 1,3-cyclopentadiene-1-carboxaldehyde, the product of photooxidation of aqueous benzene.

prompts us to report convincing evidence that the photoproduct is cyclopentadienecarboxaldehyde. This aldehyde was previously concluded[4] to be a mixture of three isomers. Using milder conditions for isolation and spectrometry, to minimize its polymerization,[4] we find its structure to be, at least very predominantly, 1,3-cyclopentadiene-1-carboxaldehyde (**1**); its anion has the fulvenoid structure **1a**. In a following communication[5] we report that oxygen is not a required reactant and discuss the role of benzvalene in formation of the aldehyde.

In accord with Farenhorst[2] we find that irradiation of benzene in aerated water yields a product which at pH 6 absorbs at 294 nm and is extractable into organic solvents and at pH 10 absorbs at 308 nm and is not extractable. Our quantum yield (0.07, calculated from extinction coefficients of 12,500 and 25,000 for the aldehyde and its anion) is similar; our product has an nmr spectrum,[6] shown in Figure 1, with corresponding resonances, but not as "single lines." In contrast, however, we find that treatment of an aqueous solution of the photoproduct with $NaBH_4$ yields not fulvene,[2] but an unsaturated alcohol[6a] with $\lambda_{max}^{H_2O}$ 248 nm, λ_{max}^{ether} 245 nm. The reduction product, which is isolable by gc,[7] exhibits a mass spectrum with a parent peak *m/e* 96 (C_6H_8O) and a fragmentation pattern indicative of a primary alcohol. Upon further reduction, with P-1 nickel boride catalyst,[8] it yields a nonabsorbing product indistinguishable (gc[7] mass spectrum) from cyclopentanemethanol.

The implication that the photoproduct is cyclopentadienecarboxaldehyde was confirmed by synthesis. The sodium salt, prepared[4] from sodium cyclopentadienide and ethyl formate, has $\lambda_{max}^{H_2O}$ 308 nm, ε ~25,000. Material purified by washing the aqueous solution with CCl_4, neutralization at 0°, extraction into CCl_4, and reextraction into alkaline D_2O exhibits an nmr spectrum at 5° with resonances at δ 6.45, 6.57, 6.83 (2 H), and 8.80 relative to external hexamethyldisiloxane (HOD at δ 5.22). Both uv and nmr spectra correspond to those observed[2] for the photoproduct anion. The presence of four olefinic protons with at least three different chemical shifts indicates that the anion has the unsymmetrical fulvenoid structure **1a**. A plausible assignment of the resonances is shown in Chart I. The aldehyde obtained by CCl_4 extraction of the neutralized anion has $\lambda_{max}^{H_2O}$ 294 nm, λ_{max}^{hexane} 278 nm,[9] as found for the photoproduct. The CCl_4 solutions exhibit the ir absorptions reported[2] for the photoproduct and an nmr spectrum identical with that in Figure 1.

Chart I



Resonances relative to internal TMS, at −20°, appear at δ 3.28 (2 H), 6.69, 6.85, 7.35, and 9.73. The fact that the area at δ 3.28 is twice that of the other resonances rules out the presence of significant amounts of 2,4-cyclopentadiene-1-carboxaldehyde. Simplification of the olefinic pattern by decoupling at δ 3.28 (these protons are coupled, $J \sim 1.5$ Hz, to each of the olefinic protons) permitted further delineation of the structure. The proton at δ 7.35, assigned to C-2 on the basis of its chemical shift, was found to be coupled to those at δ 6.69, $J = 2.1$ Hz, and at δ 6.85, $J = 1.4$ Hz; the latter are mutually coupled, $J = 5.2$ Hz. The coupling of greater than 2 Hz between protons at δ 7.35 and 6.69 suggests[10] that the latter is at C-3, rather than at C-4 or C-5. The product is therefore 1,3-cyclopentadiene-1-carboxaldehyde rather than the 1,4 isomer.

This assignment is supported by the position of the uv absorption maximum. The methyl ester of 1,3-cyclopentadiene-1-carboxylic acid, expected[11] to have an absorption maximum *ca.* 12 nm less than that of the corresponding aldehyde, has[12] λ_{max}^{hexane} 269 nm. The cross-conjugated 1,4-cyclopentadiene-1-carboxaldehyde might be expected to absorb at a much lower wavelength: the absorption maximum of thiophene-3-carboxaldehyde is 35 nm less than that of thiophene-2-carboxaldehyde.[13]

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[4] K. Hafner, G. Schultz, and K. Wagner, *Justus Liebigs Ann. Chem.*, 678, 39 (1964).

[5] L. Kaplan, L. A. Wendling, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **93**, 3821 (1971).

[6] We are indebted to Mrs. Gail Ryan and Mrs. Geraldine McDonald for these 100-MHz spectra.

(6a) NOTE ADDED IN PROOF. Conversion of this alcohol to fulvene in good yield by aqueous NaOH may account for the apparent discrepancy.

[7] Retentions of the unsaturated alcohol on Carbowax 750 at 80° relative to cyclopentanemethanol and cyclohexanol are 2.66 and 3.28, respectively.

[8] H. C. Brown and C. A. Brown, *J. Amer. Chem. Soc.*, **85**, 1005 (1963).

[9] Previously reported[4] absorption maxima at 230 and 382 nm were not present in our sample.

[10] W. B. Smith and B. A. Shoulders, *J. Amer. Chem. Soc.*, **86**, 3118 (1964).

[11] H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 218.

[12] D. Peters, *J. Chem. Soc.*, 1832 (1960).

[13] S. Gronowitz, *Ark. Kemi*, **13**, 239 (1958).

[14] Participant in the ACM Honor Semester Program, 1969.

Louis Kaplan,* L. A. Wendling,[14] K. E. Wilzbach*
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439

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