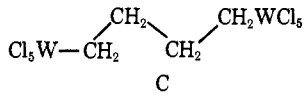
meso-isomer III gave *cis*-1,2-dideuterioethylene.[14] If the dideuterioethylenes were produced by multiple turnovers of monodeuterioethylene on the catalyst, both isomers should have given the same olefin mixture or at least some stereochemical mixing.

This stereochemical result also suggests that the intermediate must be cyclic since acyclic species such as the bimetallic intermediate C should give the opposite stereochemical results if it is assumed that the decomposition of such a product would proceed through a "Grob"-type transition state.



C

Although there are some slight differences in solvent composition, the reaction of 1,4-dilithiobutane with tungsten hexachloride produces an intermediate which yields products identical with those produced by the intermediate in the olefin metathesis reaction. All of the evidence points to the structure of this intermediate being that of a metallocycle.

The existence and position of this intermediate in an overall metathesis reaction scheme and the extension of this reaction to other metathesis catalysis are under active investigation.

Acknowledgments. The authors wish to thank Professor Donald G. Farnum for his many helpful discussions, Mr. Dale Carr for technical assistance, and the Research Corporation for partial support of this work.

(14) The 1,2-dideuterioethylenes were analyzed by infrared. Authentic samples of the cis and trans isomers were prepared by the procedure of R. S. Rabinovitch and F. S. Looney, *J. Amer. Chem. Soc.*, 75, 2652 (1953). Only trace amounts of the cis isomer could be observed in the products from the *d,l* isomer.

(15) NSF Undergraduate Research Participant, Summer 1971.

Robert H. Grubbs,* Terence K. Brunck[15]
Department of Chemistry, Michigan State University
East Lansing, Michigan 48823
Received November 23, 1971

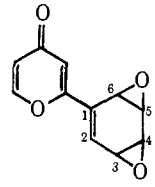
Structure of LL-Z1220. A New Antibiotic Containing a Cyclohexene Diepoxide Ring System

Sir:

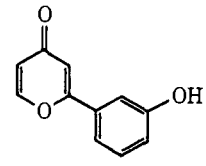
In the antibiotic program conducted in our laboratories, an undetermined fungal species was found to produce a new antibiotic, LL-Z1220,[1] for which a structure having the unique cyclohexene diepoxide ring system **1** is proposed.

When the antibiotic (colorless solid; $C_{11}H_8O_4$; mp 148° dec; $[\alpha]^{25}D$ −123° (*c* 0.591, $CHCl_3$); $\lambda_{max}^{CH:OH}$ 269 nm (ε 16,800); *m/e* 204) was treated with acetic acid–potassium iodide,[2] it yielded a deoxy compound: $C_{11}H_8O_3$; mp 241–243°; λ_{max}^{MeOH} 278 nm (ε 13,900); *m/e* 188. The ir (3380–2700 cm^{-1}) and nmr (OH singlet, 1 H, δ 9.71 in DMSO-d_6) spectra indicated the presence of one OH group in the deoxy compound. It was methylated with dimethyl sulfate in acetone containing potassium carbonate[3] and the product was oxidized with potassium permanganate.[4] A residue from a chloroform extract of the latter reaction was purified by preparative thin layer chromatography to yield crystalline *m*-methoxybenzoic acid.[5]

The $C_5H_3O_2$ moiety of the deoxy compound which was destroyed by the permanganate oxidation had a characteristic three-proton nmr pattern (δ 8.24 (1 H, d, *J* = 6.0 Hz), 6.83 (1 H, d, *J* = 2.4 Hz), 6.34 (1 H, doublet of doublets, *J* = 6.0, 2.4 Hz)). This same pattern was observed for the antibiotic[1] and was that predicted for an α-substituted γ-pyrone.[6] The antibiotic and the deoxy compound had ir absorptions near 1653 cm^{-1} as would be expected for a γ-pyrone.[7] The mass spectrum of the deoxy compound had fragmentations (M − 70) expected for an α-aryl γ-pyrone.[8] All these data are in agreement with structure **2** for the deoxy compound.



1



2

The acetic acid–potassium iodide reaction with **1** to give **2** indicated a carbocyclic six-membered ring in the $C_6H_5O_2$ portion of LL-Z1220. This reagent is known to convert epoxides to carbon–carbon double bonds; however, in this case one of the epoxides yielded a phenolic hydroxyl group. A ^{13}C nmr spectrum of the antibiotic[9] showed the presence of only one carbonyl group (13.1 ppm relative to CS_2), that was assigned to the γ-pyrone, six carbons (29.8, 34.6, 57.5, 59.5, 74.5, and 77.5 ppm) involved in double bonds, and four sp^3 carbon atoms (143.5, 143.7, 144.7, and 146.6 ppm) linked to oxygen.[10] Since by ir analysis the antibiotic contains no hydroxyl function, the two oxygens associated with the C_6 carbocyclic ring must therefore exist as ether groups. The formation of the deoxy compound **2** and a positive reaction to thiosulfate ion[11] indicate at least one of the ether oxygens exists as a conjugated epoxide and suggests **1** as a possible structure for LL-Z1220.

The antibiotic ($CDCl_3$, 100 MHz) showed three protons characteristic of the pyrone ring (δ 7.80 (1 H, d, *J* = 6.0 Hz), 6.65 (1 H, d, *J* = 2.5 Hz), 6.38 (1 H, doublet of doublets, *J* = 6.0, 2.5 Hz)), the additional olefinic

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(9) Obtained at 22.63 MHz on a Bruker HFX-90 spectrometer through the courtesy of Bruker Scientific, Elmsford, N. Y.
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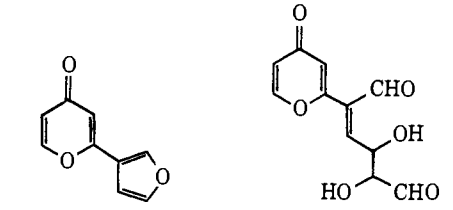
proton (δ 7.18 (doublet of doublets, J = 4.0, 1.2 Hz)), and four protons which unfortunately overlapped each other, in the region δ 4.0–3.4.

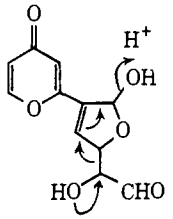
When a small amount of the shift reagent Eu(fod)$_3$ [tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione)europium(III)][12] was added, sufficient chemical shifts were induced to produce first-order multiplets which were in accord with the epoxide ring protons (the four protons were separated by 0.45, 0.59, and 0.65 ppm) in **1**. Using the indicated numbering system, the following (absolute) values for the coupling constants were measured: J_{23} = 4.0, J_{26} = 1.2, J_{34} = 2.8, J_{45} = 2.8, J_{56} = 3.4 Hz. The small J_{45} coupling constant suggests a trans configuration of epoxide groups since the dihedral angle of the corresponding protons would be ~50° for the trans and 0° for the cis arrangements.

In an effort to obtain further evidence to confirm **1**, the antibiotic was treated with acid to open the epoxide rings and then was oxidized with periodate. The resulting product had: mp 123–127°; λ_{max}^{MeOH} 277 nm (ϵ 12,300); *m/e* 162.0309 (calcd for $C_9H_6O_3$, 162.0316). The ir (1658 cm^{-1}) and the nmr (characteristic three-proton pattern) spectra indicated that this product still had the γ-pyrone ring. The remaining C_4H_3O part of the molecule had an nmr spectrum (δ 8.26, 7.72, and 6.93, each signal as an apparent one-proton doublet of doublets with J values < 2.5 Hz) expected for a β-substituted furan.[13] The periodate oxidation product was therefore assigned structure **3**. This product could be rationally derived from **1** through intermediates **4** and **5**. The furan was best obtained by dissolving the antibiotic in dilute aqueous acid and treating the resulting solutions with sodium periodate. It was not formed by acid treatment alone nor by attempted sublimation of the product from the acid treatment.



3

4



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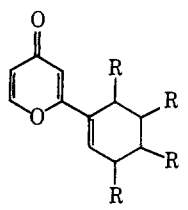

6, R = OH, OH, Cl, OCH_3

Additional evidence for structure **1** was obtained from treating the antibiotic with hydrogen chloride in methanol to obtain **6**, an expected product from the reaction of epoxide groups with this reagent.[14] The molecular formula of **6** was based on the mass spectrum which had a parent ion at *m/e* 272.04487 (calcd for $C_{12}H_{13}O_5Cl$, 272.04515) and expected chlorine isotope peaks for the parent ion and an M − 18 fragment ion. The ir and nmr spectra had adsorptions characteristic for the pyrone ring. In addition, the nmr spectrum had a doublet (δ 6.43, J = 2.3 Hz) of the olefinic proton, a system of four protons (δ 3.9–4.9) attributed to the protons on carbons bearing oxygen and chlorine, and a three-proton singlet (δ 3.55) of an OMe group. The uv spectrum, λ_{max}^{MeOH} 264 nm (ϵ 16,000), was similar to that of the starting antibiotic. The substitution pattern of the groups on the cyclohexane ring is unknown.

LL-Z1220 appears to be the first reported compound containing a cyclohexene diepoxide ring system. Recently a plant product, crotepoxide, has been reported to contain a closely related ring system, a cyclohexane diepoxide.[15] Levopimaric acid dioxide[16] and pseudoascaridole[17] are chemically modified natural products which contain cyclohexane diepoxide ring systems.

Other unique chemical features of the cyclohexene diepoxide ring system of LL-Z1220 will be reported in the near future.

Acknowledgments. We wish to thank Mr. W. Fulmor and staff for spectral data and Mr. L. Brancone and staff for elemental analyses.

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* Address correspondence to this author at Lederle Laboratories.

Donald B. Borders,* Ping Shu, John E. Lancaster
Divisions of American Cyanamid Company
Lederle Laboratories
Pearl River, New York 10965
Central Research Laboratories
Stamford, Connecticut 06904

Received December 10, 1971

Effect of Pressure on the Visible Absorption Spectrum of Metmyoglobin Fluoride

Sir:

We have investigated the effects of pressures up to 6500 kg/cm^2 on the visible absorption spectrum (450–700 mμ) of aqueous metmyoglobin fluoride. Some typical results are presented in Figure 1.

The spectrum of aqueous metmyoglobin fluoride at 1 atm (1.03 kg/cm^2) is characteristic of a high-spin hemoprotein with absorption maxima at 490 and 605 mμ.[1] Upon pressurization to 2250 kg/cm^2 there is little change in the spectrum other than an increase in absorbance due to compression of the solvent. As the pressure is further increased, however, the spectrum begins to change significantly with time. A definite equilibrium spectrum is reached eventually at each pressure. On release of the pressure to 1 atm virtually 100% return to the initial spectrum is observed. It appears that the protein undergoes a reversible change. Above 5500 kg/cm^2 the change is rapid and virtually complete and the spectrum obtained is substantially different from that observed at atmospheric pressure.

The visible spectrum of metmyoglobin fluoride at 6375 kg/cm^2 shows an absorption maximum near 540

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