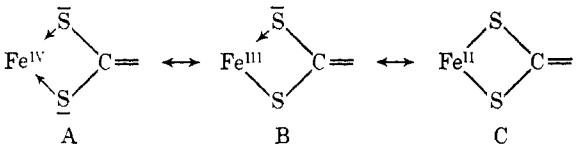



Figure 3.

Table I. Selected Structural Parameters (Å, deg) in the $Fe(DED)_3^{2-}$ Anion

| | | | |
|---|---|---|---|
| | (A) Bond Distances | | |
| M—$S_1$ | 2.289 (2) | M—$S_3$ | 2.301 (2) |
| M—$S_2$ | 2.305 (2) | | |
| $S_1$—$S_2$ (bite) | 2.786 (2) | $S_3$—$S_3'$ | 2.737 (3) |
| S···S (range of contacts | 3.226 (2)–3.744 (3) | | |
| $C_4$—$S_1$ | 1.735 (5) | $C_{11}$—$S_3$ | 1.739 (6) |
| $C_4$—$S_2$ | 1.735 (6) | | |
| $C_4$—$C_2$ | 1.369 (7) | $C_{10}$—$C_{11}$ | 1.363 (12) |
| $C_2$—$C_1$ | 1.450 (8) | | |
| $C_2$—$C_3$ | 1.487 (8) | $C_9$—$C_{10}$ | 1.485 (9) |
| $C_1$=$O_1$ | 1.215 (6) | | |
| $C_3$=$O_3$ | 1.190 (7) | $C_9$=$O_5$ | 1.196 (8) |
| | (B) Bond Angles | | |
| $S_1$—Fe—$S_2$ | 74.66 (6) | $S_3$—Fe—$S_3'$ | 72.97 (5) |
| Fe—$S_1$—$C_4$ | 89.5 (2) | | |
| Fe—$S_2$—$C_4$ | 89.0 (2) | Fe—$S_3$—$C_{11}$ | 91.6 (2) |
| $S_1$—$C_4$—$S_2$ | 106.8 (2) | $S_3$—$C_{11}$—$S_3'$ | 103.8 (2) |

the present structure are significantly shorter than those found in the high spin iron(III) tris-dithiocarbamate chelates such as the Fe(pyrrolidine-Dtc)$_3$[19] and Fe($Et_2$Dtc)$_3$,[20] at 297°K (2.41 (1) and 2.357 (5) Å, respectively). However, they are similar to those found in the structures of the low spin Fe(MePhDtc)$_3$[19] and Fe($Et_2$Dtc)$_3$[20] complexes, at 79°K (2.31 (1) and 2.306 (2) Å, respectively).

Recently a study of the metal ion and ligand dependency of the redox properties of some first-row transition metal dithiocarbamate complexes[5] was reported. The results of this study show a dependence of the oxidation potentials, for the process

$$[M(R_2Dtc)_n]^0 \rightleftarrows [M(R_2Dtc)_n]^+ + e^-$$

on (a) the R groups on the $Dtc^-$ ligands and (b) the d orbital populations of the metal ions.

The results of the present study and similar studies on the dithiocarbamate complexes indicate that the electrons removed from iron–sulfur chelates reside in molecular orbitals which involve primarily iron and sulfur functions. The relative importance of resonance forms such as those shown in Figure 3 is difficult to ascertain. However, covalency in the Fe–S bond (Figure 3b, 3c) cannot be ruled out and may well be important in the stabilization of the oxidized complexes.

**Acknowledgments.** We are grateful to the National Science Foundation and the National Institute of Health for financial support of this research.

(19) P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1163 (1972).
(20) J. G. Leipoldt and P. Coppens, *Inorg. Chem.*, **12**, 2269 (1973).
(21) Fellow of the Alfred P. Sloan Foundation and author to whom correspondence should be addressed.

**F. J. Hollander, R. Pedelty, D. Coucouvanis*[21]**
*Department of Chemistry, University of Iowa*
*Iowa City, Iowa 52242*
*Received March 18, 1974*

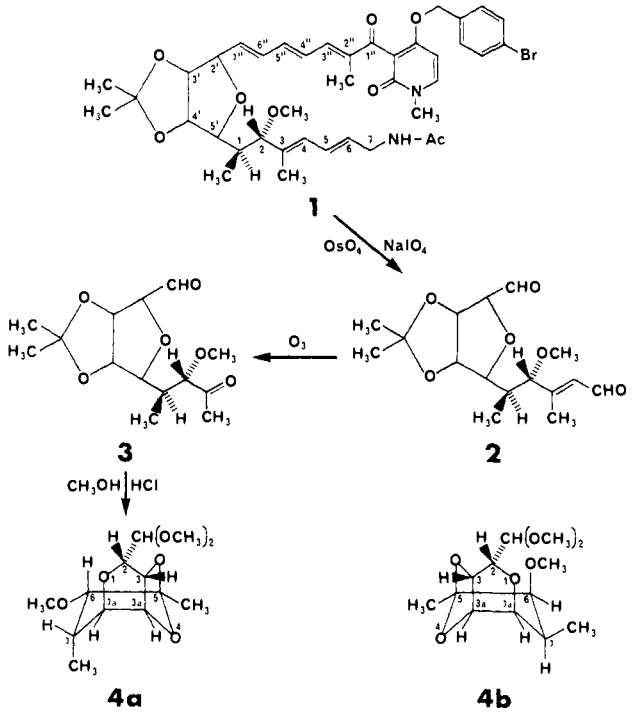
## Antibiotic X-5108. VIII. Absolute Stereochemistry of Antibiotic X-5108 and Mocimycin[1]

*Sir:*

The structure of antibiotic X-5108 including the configuration of all double bonds,[2] the chiral centers C(2) and C(3) of the octadienal derived from goldinamine[1] and corresponding to C(1) and C(2) of **1**, the absolute configuration of the goldinonyl moiety,[3] and the relative configuration of the central tetrahydrofuran ring[4] has been established. Two possible configurations of antibiotic X-5108, differing only with respect to the enantiomorphism of their tetrasubstituted tetrahydrofuran rings, remain for consideration.

To establish the chirality of the substituted tetrahydrofuran ring, we attempted to fuse a ring system containing the two known chiral centers C(1) and C(2), originating from **1**, onto the tetrahydrofuran ring and to generate a structure of sufficient conformational stability as to enable application of the Karplus relationship to the dihedral angle H–C(5′)–C(1)–H. Thus, *N*-acetyl-*O*-isopropylidenegoldinamine 4-bromobenzyl ether (**1**) was degraded (Scheme I) with a mixture of

Scheme I




osmium tetroxide and sodium metaperiodate affording dialdehyde **2** which was further cleaved with ozone to give **3**, the desired starting material for the cyclization reaction. Treatment of **3** with methanolic hydrogen chloride yielded 3,5-epoxyhexahydro-2-dimethoxymethyl-6-methoxy-5,7-dimethyl-2*H*-furo[3,2-*b*]pyran the structure of which is either **4a** or **4b**; both structures contain identical chiral centers at positions 6 and 7 derived from positions 1 and 2, respectively, of the diene

(1) Paper VII in this series: H. Maehr, J. F. Blount, M. Leach, and A. Stempel, *Helv. Chim. Acta*, **57**, 936 (1974).
(2) H. Maehr, M. Leach, L. Yarmchuk, and A. Stempel, *J. Amer. Chem. Soc.*, **95**, 8449 (1973).
(3) H. Maehr, J. F. Blount, R. H. Evans, Jr., M. Leach, J. W. Westley, T. H. Williams, A. Stempel, and G. Büchi, *Helv. Chim. Acta*, **55**, 3051 (1972).
(4) H. Maehr, T. H. Williams, M. Leach, and A. Stempel, *Helv. Chim. Acta*, **57**, 212 (1974).

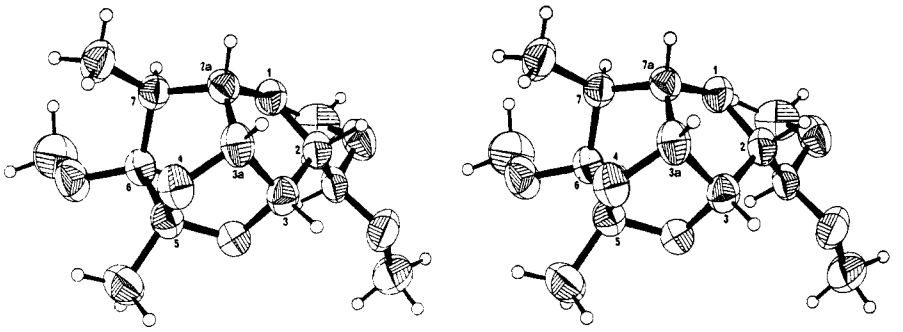


Figure 1.

side chain of **1** with the substituted tetrahydrofuran rings being related enantiomerically. Accordingly, **4a** and **4b** exhibit 7,7a-erythro and 7,7a-threo configurations, respectively, with the corresponding dihedral angles H–C(7a)–C(7)–H estimated to be 75 and 45°.

Although **4a** and **4b** fulfill the requirement of conformational stability, application of the Karplus equation did not permit a completely unequivocal choice between the two alternatives. Compounds **4a** and **4b** have no precedent as to Karplus constants, $J°$, but the selection of a $J°$ value for $0° \leqq \phi \leqq 90°$ considerably larger than 7.4 Hz appeared reasonable in view of available examples.[5] Equation $J = J° \cos^2 \phi - 0.3$ Hz, $J° = 12$ Hz, for example, led to $J_{7a,7,calcd} = 6$ Hz for $\phi = 45°$ (**4b**) and $J_{7a,7,calcd} = 0.5$ Hz for $\phi = 75°$ (**4a**). Consequently, the observed $J_{7a,7} = 1.8$ Hz suggested preference of **4a** implying a 7,7a-erythro configuration. In connection with the known chirality of C(7) in **4a** and the established relative configuration of the tetrahydrofuran ring, requiring all hydrogen substituents to be located on the same side of the ring,[4] all dissymmetric centers in **4a** would thus be defined. The inherent weakness of this analysis is due to the Karplus treatment. Although Karplus constants of $J° > 7.4$ Hz result in preference of **4a**, with $J° = 7.4$ Hz both alternatives become equiprobable whereas $J° < 7.4$ Hz tends to favor **4b**. This ambiguity is not completely unexpected and may be attributed to substituent effects and the presence of a strained ring system whereas the Karplus relationship is derived for truly tetrahedrally substituted systems.

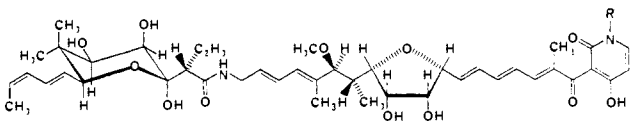
Compound **4a** was finally confirmed as the correct structure by single-crystal Roentgen analysis of **4a**, $C_{13}H_{22}O_6$, mp 98°, $\alpha D$ + 15° (*c* 1.0, dioxane), *m/e* (%) 274 (3), 75 (100), space group $P2_1$ with unit-cell dimensions $a = 7.503$ (4) Å, $b = 8.726$ (5) Å, $c = 11.268$ (7) Å, $\beta = 103.17$ (4)°, and $d_{calcd} = 1.268$ g cm$^{-3}$ for $Z = 2$. Analysis was based on 1354 reflections with intensities significantly greater than background ($I > 2.5\ \sigma(I)$) which were part of 1604 accessible reflections with $\theta < 76°$.

The structure was elucidated by a multiple solution procedure.[6] Refinement of data was carried out by full-matrix least squares. Anisotropic thermal parameters were used for all atoms except hydrogen atoms. The final discrepancy index, *R*, is 0.039. A stereodrawing of **4a** is shown in Figure 1.

(5) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, p 280 ff.

(6) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **26**, 274 (1970).

With the structure of **4a** established it is now possible to present the structure of antibiotic X-5108 in full stereochemical detail as shown in **5a**.



**5a**: R = $CH_3$ (Antibiotic X-5108)
**5b**: R = H (Mocimycin)

We have previously demonstrated that mocimycin can be regarded as des-*N*-methyl antibiotic X-5108 (**5b**); the evidence of chiral identities of the two antibiotics was elaborated by establishing identity of essential degradation products.[2] As additional proof of chiral parity of **5a** and **5b**, we now obtained **4a** from mocimycin *via* **2** and **3**. Compound **4a** derived from mocimycin exhibited melting point, optical rotation, and ir and nmr spectra identical with those of **4a** derived from **5a**. The structure of mocimycin is thus established as **5b**.

**Hubert Maehr,* Michael Leach**
**John F. Blount, Arthur Stempel**
*Chemical Research Department, Hoffmann-La Roche, Inc.*
*Nutley, New Jersey 07110*
*Received March 22, 1974*

## Substituent Effects on the Intrinsic Acidities of Benzoic Acids Determined by Gas Phase Proton Transfer Equilibria Measurements

*Sir:*

Quantitative correlations of reaction rates and equilibria, particularly in the form of linear free energy relationships, have played a central role in physical organic chemistry. These studies were initiated by the Hammett acidity plot in which the free energy changes for proton transfer from benzoic to substituted benzoic acids in aqueous solution were used as a standard scale. Hammett's work was followed by very substantial experimental and interpretative development. However, some problems have remained. Many of these are connected with the difficulty of assessing the effect of the solvent. Therefore it is of importance to obtain substituent energy differences for the isolated molecules. The present work describes such measurements. The proton transfer equilibria (1) were ob-

$$A_1^- + A_2H = A_1H + A_2^- \quad (1)$$