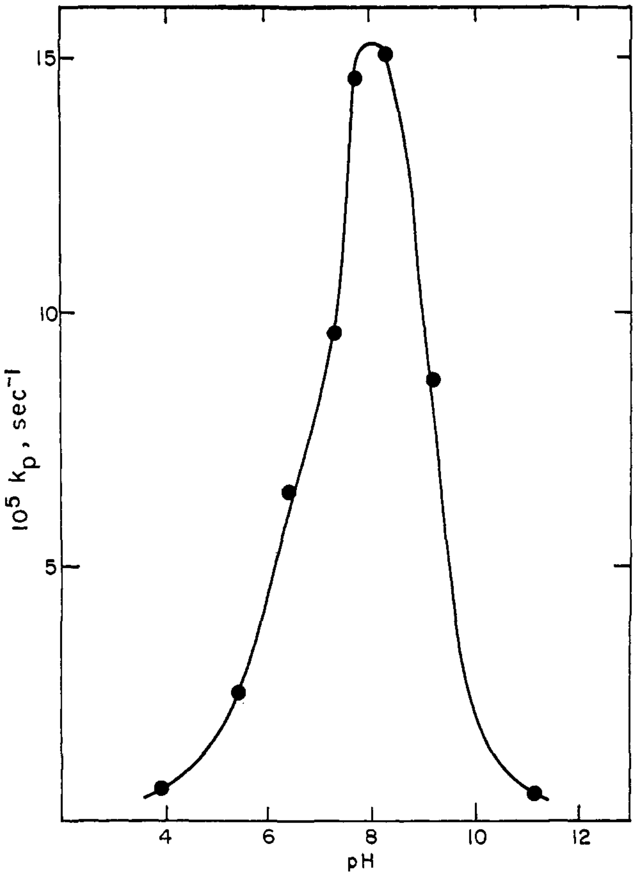

Figure 2. First-order rate constants for the dedeuteration of 0.053 *M* isobutyraldehyde-2-*d* in the presence of 0.97 ± 0.03 *N* PEI-1800 at 35°.

the intermediate iminium ions are dedeuterated intramolecularly.

Studies using 0.053 *M* isobutyraldehyde-2-*d* and 0.97 *N* PEI-1800 at various pH values showed (see Figure 2) that the rate of dedeuteration is at a maximum around pH 8. This observation is readily explained in terms of the proposed reaction mechanism. If the reaction solution is too basic, not enough of the imines are protonated to give iminium ions; if the solution is too acidic, the remaining free amino groups are too few and too weakly basic to provide effective internal catalysis.

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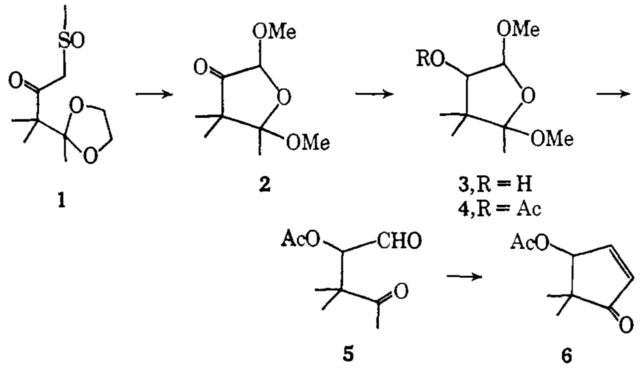
Total Synthesis of *dl*-Illudin M

Sir:

Among a number of fungus sesquiterpenoids,[1] illudin[2] M and S (lampterol)[3] are the first to be shown possessing a new skeleton biogenetically[4] related to humulene. We wish to report here completion of a stereospecific total synthesis of illudin M.

Ethyl dimethylacetoacetate ethylene ketal, bp 110° (17 mm), $C_{10}H_{18}O_4$,[5] was converted by methylsulfinyl carbanion to a β-keto sulfoxide (**1**), mp 53–56°, $C_{10}H_{18}O_4S$, following Corey's method.[6] On treatment with iodine in methanol,[7] **1** yielded an epimeric pair of tetrahydrofuranones (**2**)[8] which was reduced by sodium borohydride to an isomeric mixture of tetrahydrofuranols (**3**).[8] On being dissolved in diluted hydrochloric acid, the acetates of the mixture **3** gave a ketoaldehyde (**5**) (ir 1735, 1705, and 1230 cm^{-1}; nmr τ 8.75 (6 H) s, 7.89 (6 H) s, 5.1 (1 H) s, and 0.5 (1 H) s; bisdinitrophenylhydrazone mp 201–202°; $C_{21}H_{22}N_8O_8$) which was then cyclized to a cyclopentenone (**6**)[9] by refluxing with sodium hydride in benzene.

The unsaturated ketone **6** affords, on treatment with the β-keto sulfoxide **7**[10] under Michael conditions, stereoselectively the single product **8**, as reported earlier.[9] The Pummerer rearrangement[11] converted **8** to a ketone (**9**)[10] which, on being simply heated in ethanol, afforded a single methyl ketone (**10**), mp 134–135°; $C_{19}H_{28}O_7S$ (ir 3320, 1745, and 1695 cm^{-1}; nmr τ 9.0, 8.85, 7.7, 7.8, and 7.85, each (3 H) s, 5.9–6.4 (4 H) m, and 4.6 (1 H) d (J = 9 Hz)). On treatment with potassium *t*-butoxide, **10** yielded a cisoid enone **11**, mp 154–155°, $C_{19}H_{26}O_6S$ (ir 3460, 1730, 1710, 1685, 1620, and 1250 cm^{-1}; nmr τ 8.95, 8.8, 7.9, and 7.85, each (3 H) s, 7.95 (3 H) d (J = 2 Hz), 4.35 (4 H) broad t, and 4.4 (1 H) d (J = 9 Hz)) which was converted to an acetate (**12**). Attack of methylmagnesium iodide occurred selectively at the six-membered ketone of **12** and, moreover, stereoselectively afforded **13**,[12] mp 140.5–141°, $C_{22}H_{32}O_7S$ (ir 3450, 1745, 1705, 1615, and 1235 cm^{-1}; nmr τ 8.97, 8.81, 8.62, 7.86, 7.84, and 7.82, each (3 H) s, 8.03 (3 H) d (J = 2 Hz), 7.39 (1 H) s, 6.6 (1 H) m,



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[1] Marasmic acid: J. J. Dugan, P. de Mayo, M. Nisbet, J. R. Robinson, and M. Anchel, *J. Am. Chem. Soc.*, **88**, 2838 (1966); illudol: T. C. McMorris, M. S. R. Nair, and M. Anchel, *ibid.*, **89**, 4562 (1967); fomannosin: J. A. Kepler, M. E. Wall, J. E. Mason, C. Basset, A. T. McPhail, and G. A. Sim, *ibid.*, **89**, 1260 (1967); hirsutic acid: F. W. Comer, F. McCapra, I. H. Qureshi, and A. I. Scott, *Tetrahedron*, **23**, 4761 (1967).

[2] T. C. McMorris and M. Anchel, *J. Am. Chem. Soc.*, **87**, 1594 (1965).

[3] T. Matsumoto, H. Shirahama, A. Ichihara, Y. Fukuoka, Y. Takahashi, Y. Mori, and M. Watanabe, *Tetrahedron*, **21**, 2671 (1965).

[4] W. Parker, J. S. Roberts, and Ramage, *Quart. Rev.* (London), **21**, 331 (1967).

[5] All new compounds indicated by molecular formulas gave satisfactory analytical data.

[6] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1345 (1965).

[7] β-Keto sulfoxides in general give α-keto acetals on treatment with iodine in methanol: T. L. Moore, *J. Org. Chem.*, **32**, 2786 (1967).

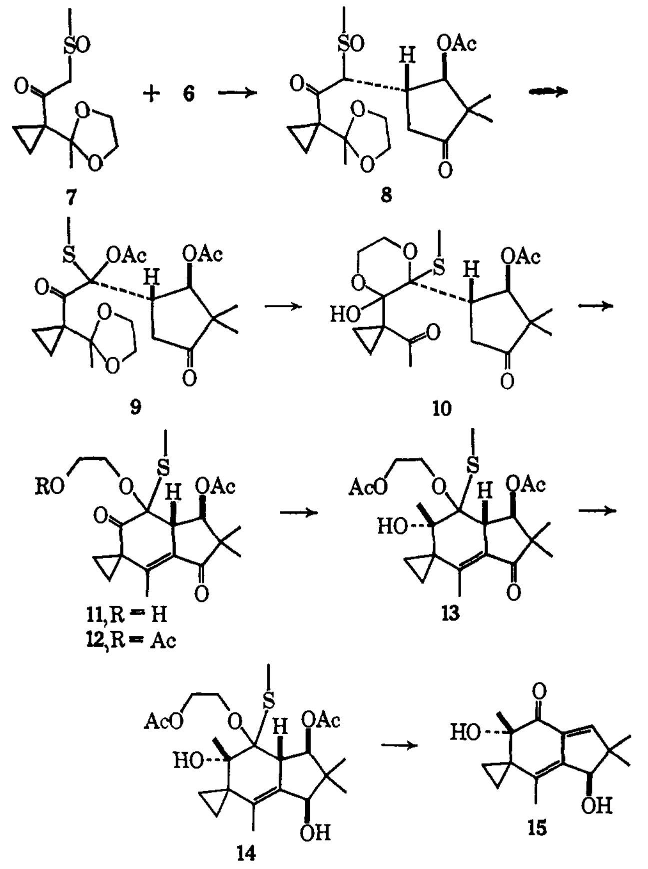
[8] Although these compounds were obtained as isomeric mixtures, the depicted structures are fully supported by nmr and ir spectroscopic observations.

[9] T. Matsumoto, H. Shirahama, A. Ichihara, H. Shin, S. Kagawa, N. Ito, T. Hisamitsu, T. Kamada, F. Sakan, K. Saito, S. Nishida, and S. Matsumoto, *Tetrahedron Letters*, 1925 (1968).

[10] T. Matsumoto, H. Shirahama, A. Ichihara, H. Shin, S. Kagawa, N. Ito, T. Hisamitsu, T. Kamada, and F. Sakan, *ibid.*, 4097 (1967).

[11] L. Horner and P. Kaiser, *Ann. Chem.*, **626**, 19 (1959).

[12] The stereochemistry of **13** shown is based on an analogy. See ref 9.



5.7 (4 H) m, and 4.6 (1 H) d (J = 9 Hz)). The hemithioketal **13** was reduced by sodium borohydride in tetrahydrofuran to give a single diol (**14**) (ir 3450, 1740, and 1640 cm^{-1}) which was finally converted to *dl*-illudin M (**15**), mp 120–122.5°, by treatment with mercuric chloride in aqueous acetone. The infrared spectrum ((CCl_4) 3590, 3460, 1690, 1650, and 1605 cm^{-1}) and R_f values on tlc of the product were perfectly identical with those of the natural product in all respects.

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Preparation and Structural Characterization of Six-Coordinate Iron(III) Complexes Containing the Fe–S–S Linkage

Sir:

Current interest in the structure–function relationship in nonheme iron proteins (NHIP) containing iron–sulfur bonds[1,2] has led us to investigate various aspects of the coordination chemistry of iron with sulfur donor ligands. One intriguing feature of certain NHIP is the presence of a sulfur atom, the so-called "inorganic" or "acid-labile" sulfur, which is chemically distinct from cysteine sulfur and is required in a 1:1 mole ratio with iron in order for the protein to have biological activity. Two previously suggested alternative structural roles for this sulfur atom are (1) to link two or more iron atoms in linear chains[3] and (2) to participate in an iron–disulfide linkage with a sulfur atom from cysteine (cyst-S-S-Fe).[2] Although there is considerable precedent for sulfide-bridged metal atoms in inorganic chemistry, little information is available on metal–disulfide linkages.[4] The present note reports the preparation and structural characterization of six-coordinate iron complexes containing R-S-S-Fe bonds.

When tetrahydrofuran solutions containing Zn(TTD)$_2$[5,6] were treated with ferric chloride dissolved in methanol, black crystals were obtained. After recrystallization from carbon disulfide–petroleum ether, analysis of the complex indicated the formula Fe(TTD)$_2$(DTT).[6] *Anal.* Calcd for $C_{24}H_{21}S_8Fe$: C, 46.4; H, 3.38. Found: C, 46.7; H, 3.57. Treatment of chloroform solutions of this compound with triphenylphosphine[7] yielded, in addition to triphenylphosphine sulfide, complexes Fe(TTD)(DTT)$_2$ and Fe(DTT)$_3$·$CHCl_3$. *Anal.* Calcd for $C_{24}H_{21}S_7Fe$: C, 48.9; H, 3.59. Found: C, 48.2; H, 3.58. Calcd for $C_{24}H_{21}S_6Fe \cdot CHCl_3$: C, 44.3; H, 3.25. Found: C, 44.3; H, 3.41. All complexes were found to have room-temperature magnetic moments in the range expected for low-spin Fe(III), 2.2–2.5 BM, and display contact-shifted proton nmr spectra. The nmr spectrum of Fe(DTT)$_3$·$CHCl_3$ in CS_2 provided confirmatory evidence for the chloroform of solvation. The results of a detailed analysis of the spectral and magnetic properties of these compounds will be reported later; here we summarize the important structural features of the representative complex Fe(TTD)(DTT)$_2$, as determined by a single-crystal X-ray diffraction study.

Crystals of the mixed ligand complex were found to have Laue symmetry 2/m with lattice constants a = 18.24 ± 0.03, b = 7.64 ± 0.02, c = 24.11 ± 0.03 Å, β = 125.4 ± 0.1°. From the measured density, ρ = 1.42, and observed systematic absences, $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, the space group was ascertained to be $P2_1/c$ with four molecules per unit cell. The density calculated on the basis of the formula $C_{24}H_{21}S_7Fe$ is 1.43. Intensity data were collected by the equiinclination Weissenberg technique for successive layers $h0l$–$h6l$ using Cu Kα radiation. The visually estimated intensities were then corrected for absorption and LP effects, placed on a common scale by Wilson's method, and used to compute a three-dimensional Patterson map. Solution of the Patterson revealed the location of the iron and several sulfur atoms, which provided sufficient phasing for the complete structure determination in subsequent Fourier and least-squares refinement

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(1) A. San Pietro, Ed., "Non-Heme Iron Proteins: Role in Energy Conversion," Antioch Press, Yellow Springs, Ohio, 1965.

(2) R. Malkin and J. C. Rabinowitz, *Ann. Rev. Biochem.*, **36**, 113 (1967).

(3) D. C. Blomstrom, E. Knight, Jr., W. D. Phillips, and J. F. Weiher, *Proc. Natl. Acad. Sci., U. S.*, **51**, 1085 (1964).

(4) J. Weiss, *Fortschr. Chem. Forsch.*, **5**, 635 (1966); J. Weiss and H. Neubert, *Z. Naturforsch.*, **21b**, 286 (1966).

(5) Abbreviations used in this paper are as follows: TTD = thio-*p*-toluoyl disulfide, $CH_3C_6H_4CS_3^-$; DTT = dithio-*p*-toluate, $CH_3C_6H_4CS_2^-$; MNT = 1,2-dicyano-1,2-ethylenedithiol.

(6) J. P. Fackler, D. Coucouvanis, J. Fetchin, and W. C. Seidel, *J. Am. Chem. Soc.*, **90**, 2784 (1968). In this reference it is noted that "Zn(TTD)$_2$" shows variable sulfur content on titration with triphenylphosphine and may in fact contain some Zn(TTD)(DTT) or Zn(DTT)$_2$.

(7) D. Coucouvanis and J. P. Fackler, Jr., *ibid.*, **89**, 1346 (1967); J. P. Fackler, Jr., and D. Coucouvanis, *ibid.*, **89**, 1745 (1967).