

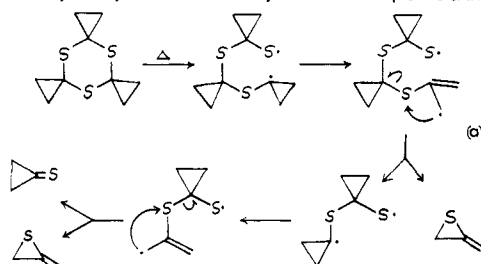
the two CD₂ species, give the following structural parameters (see Figure 1): C₁—S, 1.732 (2), C₂—S, 1.849 (1), C₁—C₂, 1.454 (5), C₁=C₃, 1.333 (2), C₂—H, 1.084 (1) Å; ∠C₁SC₂, 47.8 (1), ∠SC₁C₂, 70.3 (1), ∠SC₂C₁, 61.9 (1), ∠C₃C₁C₂, 146.2 (3), ∠HC₂H, 116.4 (1)°, and (assuming a symmetrical HC₂H groups), C₃—H, 1.081 (1) Å and ∠C₁C₃H, 120.5 (2)°. The HC₂H plane is displaced from the SC₂C₁ angle bisector plane by an angle of 7.2° bringing these hydrogens closer to the S atom. The dipole moment of **3** is 1.36 (2) D.

The mechanism proposed in eq 2 to account for the scrambling of ¹³C and deuterium labeling in **3** is consistent with the long, and presumably weakened, C₂—S bond in **3**.^{23,24} Allene episulfide has a gas-phase lifetime varying from ~3 min (room temperature) to ~20 min (dry ice temperature) at ~0.05 Torr and may be revitalized after condensation at -196 °C. Efforts are currently underway to define more precisely the equilibrium of eq 1 by experimental as well as theoretical methods and to synthesize cyclopropanethiones by nonpyrolytic routes.²⁶

Acknowledgment. We gratefully acknowledge support for this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society (E.B.), the North Atlantic Treaty Organization (E.B.), the Research Corporation (R.E.P.), the National Science Foundation under its Undergraduate Research Participation program, and the University of Missouri—St. Louis. We thank Professor A. G. Hortmann for samples and helpful discussions.

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- (1) (a) Flash Vacuum Pyrolysis Studies. 6. (b) Part 5: R. E. Penn, E. Block, and L. K. Revelle, *J. Am. Chem. Soc.*, **100**, 3622 (1978). (c) Presented at the 12th Midwest Regional Meeting of the American Chemical Society, Kansas City, Mo., Oct 31, 1976, at the 174th ACS National Meeting of the American Chemical Society, Chicago, Ill., Aug 31, 1977, Abstracts ORGN 90, and at the 8th International Symposium on Organic Sulfur Chemistry, Portoroz, Yugoslavia, June 18–23, 1978.
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- (6) (a) A. I. Meyers and M. E. Ford, *J. Org. Chem.*, **41**, 1735 (1976). (b) The exo-endo stereochemistry of the thirane ring has not been assigned; mechanistic considerations suggest that sulfur should be in the exo position.
- (7) All new compounds have been fully characterized.
- (8) (a) Trithianes are known to be thermal precursors of thiocarbonyl compounds: D. R. Johnson, F. X. Powell, and W. H. Kirchhoff, *J. Mol. Spectrosc.*, **39**, 136 (1971); P. S. Fraser, L. V. Robbins, and W. S. Chilton, *J. Org. Chem.*, **39**, 2509 (1974). (b) For a recent review of retro-Diels–Alder reactions of compounds related to **5**, see J. L. Ripoll, A. Rouessac, and F. Rouessac, *Tetrahedron*, **34**, 19 (1978).
- (9) Although the microwave spectrum of **1** is now unknown, the reasonable range within which spectral absorption should occur can be confidently predicted from the microwave spectral and structural data on cyclopropanone (J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Am. Chem. Soc.*, **91**, 1896 (1969)) and the assumption that the C=S distance in **1** is greater than the C=O distance in cyclopropanone by 0.40 ± 0.05 Å.
- (10) Prepared using the lithio-2-(methyl-¹³C-thio)- or lithio 2-(methyl-*d*₂-thio)-2-oxazoline reagent **6** prepared by using methyl-¹³C- or -*d*₂ iodide and the procedure of Meyers.^{6a}
- (11) Alternatively **3** may be formed directly from **4** via sequence a through ring



- opening of intermediate cyclopropyl radicals to allyl radicals (a process known to be very facile¹²), followed by homolytic displacement at sulfur. The last step of this sequence affords **1**.
- (12) K. S. Chen, D. J. Edge, and J. K. Kochi, *J. Am. Chem. Soc.*, **95**, 7036 (1973).
 - (13) The pyrolysis of **4**, **5**, **7**, and **8** also affords CS₂ which we suggest may arise from CS via a sulfur-abstraction step.
 - (14) Assuming bond strengths of 129 kcal mol⁻¹ for C=S,¹⁵ 146 kcal mol⁻¹ for C=C, 74 kcal mol⁻¹ for C—S,¹⁵ and 83 kcal mol⁻¹ for C—C, and assuming that the value for the difference in strain energy between cyclopropane and thirane (8 kcal mol⁻¹)¹⁵ is a good approximation of the difference in strain energy between **1** and **3**, it is found that **3** is 7 kcal mol⁻¹ more stable than **1**. Applying the same analysis to cyclopropanone–allene oxide, one finds that cyclopropanone is 22 kcal mol⁻¹ more stable than allene oxide.
 - (15) S. W. Benson, *Chem. Rev.*, **78**, 23 (1978).
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 - (17) P. F. Hudrlik, A. M. Hudrlik, and C.-N. Wan, *J. Org. Chem.*, **40**, 1116 (1975).
 - (18) Kindly supplied by A. G. Hortmann and A. Bhattacharjya. See A. Bhattacharjya, Ph.D. Thesis, Washington University, 1976. Bhattacharjya was unsuccessful in isolating allene episulfide on bulk pyrolysis of **8**.
 - (19) Prepared by reaction of cyclopropanethiol²⁰ with allyl bromide (**9a**⁷), oxidation of cyclopropanethiol with I₂ (**9b**⁷), and reaction of dicyclopropyl disulfide (**9b**) with chlorine (**9c**⁷).
 - (20) L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **89**, 593 (1970).
 - (21) A microwave study of thioacrolein has been briefly reported (H. W. Kroto, "Sixth Austin Symposium on Gas Phase Molecular Structure," Austin, Texas, 1976, Paper MA4) but detailed results have not yet reached print. Independent assignment in this laboratory of the normal isotopic species (A = 45.8 × 10³, B = 2796.0, and C = 2635.3 MHz) as well as several isotopic modifications serve to identify thioacrolein beyond question.
 - (22) Twice the standard deviations are given throughout as a measure of the uncertainty in the structural parameters. Owing to the proximity of the central carbon to a principal inertial axis, the C₁—C₂ distance has a systematic uncertainty which could be as large as ±0.015 Å.
 - (23) The C—S bond distance in thirane is 1.819 Å: R. L. Shoemaker and W. H. Flygare, *J. Am. Chem. Soc.*, **90**, 6263 (1968).
 - (24) A similar lengthening of the S—C (saturated) distance is seen in α-thio-lactones^{25a} and thiranimines.^{25b}
 - (25) (a) E. Schaumann and V. Behrens, *Angew. Chem., Int. Ed. Engl.*, **16**, 722 (1977); (b) G. L'abbe, J.-P. Dekerk, J.-P. Declercq, G. Germain, and M. Van Meerse, *ibid.*, **17**, 195 (1978).
 - (26) Following submission of this work a report appeared (E. Jongejan, Th. S. V. Buys, H. Steinberg, and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **97**, 214 (1978)) describing the formation of allene episulfide by pyrolysis of 8,9-dioxo-4-thiadispiro[2.1.2.3]decan-9-one. Allene episulfide, characterized by its ¹H and ¹³C NMR, IR, UV, and mass spectra, is reported to be stable in dilute solution at -30 °C for several hours. Byproducts of the pyrolysis include allene, carbon disulfide, and ethylene, which products are suggested (as we have) to arise from fragmentation of cyclopropanethione.
 - (27) National Science Foundation Undergraduate Research Participant, 1976.

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Lychnopholic Acid, a Novel Trioxxygenated Caryophyllene Derivative from *Lychnophora affinis* Gardn.¹

Sir:

Intense interest during the past 10 years in cytotoxic, potentially antitumor-active natural products has led to the isolation and characterization of many sesquiterpenoids having, very frequently, multiple oxygenated functional groups in chemically interesting contiguous arrays.² These compounds generally belong to the eudesmane, germacrane, guaiane, and pseudoguaiane subfamilies of sesquiterpenoids. Other classes of sesquiterpenoids, however, seem for unknown reasons to have very few oxygenated representatives; in particular, the only oxygenated caryophyllenes hitherto known appear to be caryophyllene oxide (**1**), caryophyllenol I and II (**2** and **3**, respectively),³ α-multijugenol, which is isomeric with **2** and **3**,⁴ and the nor derivatives kobusone (**4**) and isokobusone (**5**).⁵ We now report the novel structure **6** (relative configuration) for lychnopholic acid, a noncytotoxic constituent of *Lychnophora affinis* Gardn. (Compositae), a plant originally under investigation in our laboratory⁶ for its cytotoxic constituents.

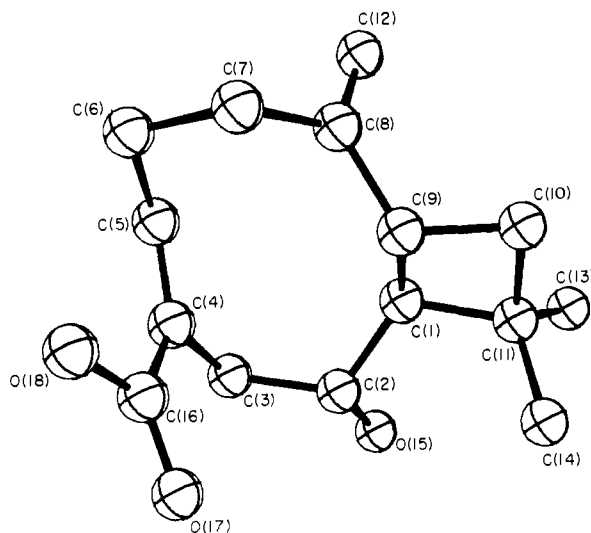
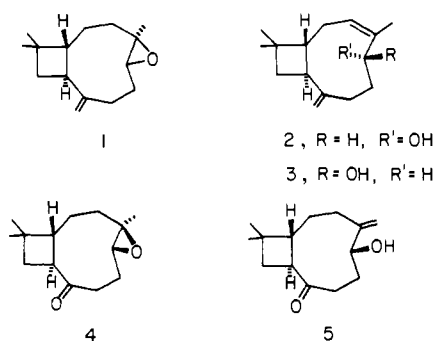


Figure 1. A computer generated perspective drawing of lychnopholic acid.



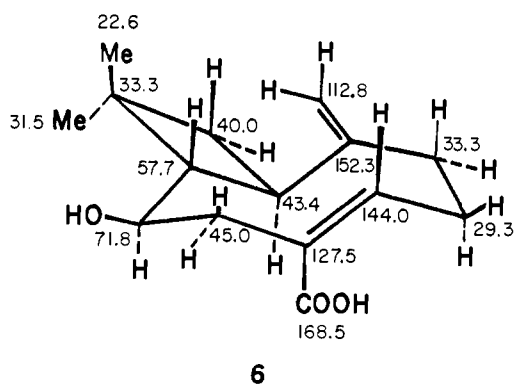
Lychnopholic acid (M^+ : 250.1558; calcd for $C_{15}H_{22}O_3$, 250.1563) showed ν_{\max} (KBr) 3360, 2580, 1675, and 1630 cm^{-1} , which suggested an α,β -unsaturated carboxyl group. 1H NMR spectra at 60 MHz further indicated an exocyclic methylene group and a *gem*-dimethyl group. Lychnopholic acid is therefore bicyclic. Since the spectral data at this stage suggested a hydroxy acid derived probably, although not certainly, from caryophyllene or himachalene, an X-ray structure determination was undertaken.

A clear crystal of lychnopholic acid, 0.75 mm \times 0.4 mm, belonged to the monoclinic space group $C2$ with calculated and observed density of 1.14 g/cm^3 for two molecules of $C_{15}H_{22}O_3$ in the asymmetric unit. Cell constants, determined by centering 15 reflections at low temperature ($\approx -60^\circ C$), were $a = 25.478$ (7) \AA , $b = 7.302$ (3) \AA , $c = 19.512$ (6) \AA , and $\beta = 126.46$ (2°). All data were measured at low temperature on a fully automated diffractometer using a ω -scan technique at a minimum scan rate of $1^\circ/min$, and Cu $K\alpha$ radiation (1.54178 \AA). All unique reflections with $2\theta \leq 114^\circ$ were measured and, after correction for Lorentz, polarization, and background effects, 1882 of 2152 unique reflections (87.45%) were judged observed ($F_o^2 \geq 3\sigma F_o^2$). The structure was solved by a multiple-solution tangent formula method and refined by full-matrix least squares.⁷ Heavy atoms were assigned anisotropic temperature factors and all hydrogens were identified and refined isotropically. The standard crystallographic residual for the complete structure was 0.037.

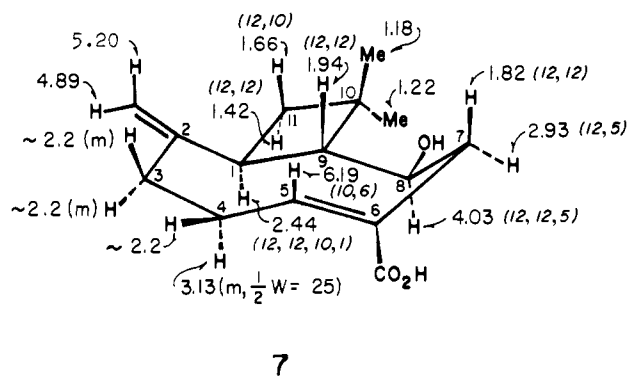
The result of the X-ray diffraction experiment, which defines only the relative stereochemistry of lychnopholic acid, is shown in Figure 1. Lychnopholic acid crystals contain two molecules in the asymmetric unit, but there is no substantial difference in the conformation of these. In general, bond distances and angles agreed with generally accepted values. Further crys-

tallographic details can be found in the supplemental material.⁸

The unique structure of lychnopholic acid, in particular the presence of both polar functions on the nine-membered ring, prompted a detailed study of the NMR spectra. A ^{13}C NMR study of lychnopholic acid (in $CDCl_3$ containing a trace of Me_2SO-d_6 to facilitate solution of the compound) was performed employing the techniques of PND, off-resonance decoupling, single-frequency decoupling, and partially relaxed Fourier transform.⁹ This disclosed the nature of all 15 carbon atoms (see 6). Extensive decoupling experiments utilizing the



1H NMR spectra at 100 and 220 MHz clarified the interconnection of the contiguous proton system, and independently demonstrated the trans fusion of the cyclobutane ring to the nine-membered ring as well as the trans configuration of the endocyclic double bond. The 1H NMR results are summarized in structure 7. The NMR data also suggest that the solution conformation of lychnopholic acid is quite similar to that adopted in the solid state.



Further derivatives of caryophyllene related to lychnopholic acid have recently been obtained from *L. affinis* in our laboratory; these will be described in a full paper. We await the isolation of related compounds from other sources in order to begin an assessment of their phytochemical significance.

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References and Notes

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- (8) Fractional coordinates, bond distances, bond angles, and observed and calculated structure factors are available as a supplement to publication. To obtain a microfiche copy of the supplement to publication, contact the Photo Service, Iowa State University, Ames, Iowa 50011, requesting the Supplement to Publication for this article and submitting \$0.50 in the form of cash, check, or money order. Give your name and complete address (including zip code) for mailing.
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Matrix Isolation Study of FeMn Molecules

Sir

Recently the matrix isolation technique has been used in conjunction with the Mössbauer effect to study "almost free" atoms and molecules.^{1,2} The main purpose of those experiments was to determine the isomer shift (IS) calibrations. By modifying the matrix isolation technique so that poor isolation is obtained, one may produce dimer and higher aggregate species which are of great interest in areas such as nucleation, surface physics and chemistry, alloying, and heterogeneous catalysis.³ The first stage in these studies should be to examine the simplest molecules, the homonuclear diatomic molecules. There have been several studies of diatomic molecules both in the gas phase and isolated in rare gas solids.⁴ Several studies of heteronuclear diatomic molecules using different spectroscopic techniques have been published by various groups.⁵ In this work we want to report a Mössbauer study of matrix isolated iron-manganese molecules. From the Mössbauer parameters we are able to determine the electronic ground state of the FeMn molecule.

The samples were made in a liquid-helium cryostat evacuated to a pressure of $<10^{-7}$ Torr. The Mn and (90% enriched) ⁵⁷Fe atomic beams were produced in alumina crucibles contained in resistance heated tantalum furnaces and codeposited with a stream of Ar gas at ~ 4.2 K onto a Be disk: the rare gas deposition rate being monitored by the attenuation of the

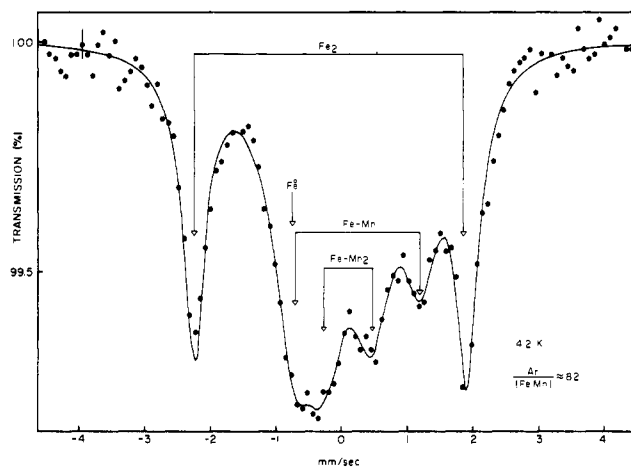


Figure 1. Mössbauer spectrum of (FeMn)-Ar at 4.2 K, 1.2 at. % metal concentration (continuous line is the fit to the experimental data).

6.3-keV X-ray of a ⁵⁷Co/Pd source, the metal deposition rates being calculated through previously determined collection efficiencies. Mössbauer spectra were obtained with a conventional constant acceleration spectrometer using the same source as above. An iron foil was used for calibration purposes and the zero velocity is given with respect to this absorber. Mössbauer spectra were taken for two different metal concentrations, 1.2 and 3 at. % metal in argon. The spectra were analyzed using a nonlinear least-squares fitting program and assuming Lorentzian line shapes.

The Mössbauer spectrum for the 1.2 at. % metal sample is shown in Figure 1. The Fe:Mn ratio for this sample was $\sim 1:1$. In this figure the presence of iron monomers and iron dimers (Fe₂) can be easily identified by their respective IS, -0.75 mm/s for Fe⁰ and -0.14 mm/s for Fe₂.¹ The iron dimer also has a characteristic quadrupole splitting (QS) of 4.09 ± 0.03 mm/s. The best fit to the spectrum is obtained when two extra doublets are considered. One has an IS of 0.24 ± 0.03 mm/s and a QS of 1.93 ± 0.03 mm/s and is indicated in Figure 1 as FeMn. The identification of this doublet as FeMn comes from its concentration dependence, the magnitude of the QS and IS, and its comparison with the values obtained for FeNi⁶ (QS = 1.95 ± 0.03 mm/s, IS = -0.54 ± 0.03 mm/s). One major difference between the FeNi and the FeMn molecules is that the latter has a more positive IS. The relative iron concentration in the argon matrix was 0.5 at. %, and no iron trimers are detectable using Mössbauer spectroscopy at this iron concentration.^{1,6}

There is another doublet in Figure 1 that we have tentatively identified as FeMn₂ (and/or Fe₂Mn). This doublet is characterized by an IS = 0.10 ± 0.03 mm/s and a QS = 0.74 ± 0.03 mm/s. The ratio of the areas of the two doublets was $\sim 1:1$, with the line width for the triatomic molecule equal to 0.76 mm/s, broader than that of FeMn and Fe₂. This broadening of the line suggests different geometrical configurations for the triatomic molecule. However, both Fe₂Mn and FeMn₂ are equally probable at the concentration used and the broadening of the lines could be produced by slightly different IS and QS for the two molecules.

In order to further study the concentration dependence of the iron-manganese molecules, we carried out measurements at a higher metal to argon ratio (metal/argon, 1:30). In this case the ratio of iron to manganese was 1:3 and consequently the only pure iron species we were able to observe were Fe⁰ and Fe₂; however, larger multimers of iron-manganese are possible. Trimers and higher multimers of iron become detectable by Mössbauer spectroscopy only at concentrations higher than 1.5 at. %; consequently the contribution of Fe₃ to the spectrum in Figure 2 is negligible. However, Fe₃ may appear after an