sorption spectra of **3** and **4** at 77°K.[12-14] Both spectra showed similar characteristics and suggested both carbenes had the similar π-electronic configuration. Carbene **3** (468 mμ) absorbed at longer wavelengths than did **4** (486 mμ), consistent with the smaller D value of **3** than that of **4**.

The smaller D value in **1** is due to the delocalization of the electron on C-1 with the π system of the aromatic rings. From the E/D ratio, the angle for **1** was also determined to be ~150°; this value is larger than that of the internuclear angle of the seven-membered ring.[15] This suggests that the seven-membered ring is almost in a plane similar to that of tropylium ion.

Because of the dominance of the one-center interaction, for a given geometry about C-1, D should be approximately proportional to the π spin density at C-1, ρ_1.[16] A HMO calculation gives 0.34, 0.37, 0.40, and 0.40 for the dibenzo[*a,d*]cycloheptenyl, fluorenyl, diphenylmethyl, and dihydrodibenzo[*a,d*]cycloheptenyl radicals, respectively. These π spin densities are parallel to the D values of corresponding carbenes. On the other hand, tribenzo[*a,c,e*]heptenyl radical yields $\rho_1 = 0.09$, while the D value of **2** is larger than those of **1**, **3**, and **4**. This may be due to the substantial steric hindrance to coplanarity of **2**. A similar effect of phenyl groups was observed for the pK_{R^+} of tribenzotropylium cation. Generally, a plot of pK_{R^+} values *vs.* the π-energy difference between a model of the carbinol and that of the cation gives a linear correlation. However, a deviation is observed for tribenzotropylium cation.[17]

The carbenes **1** and **2** added to olefins in a stereospecific manner, although the ground state of these carbenes is triplet. The mechanistic discussion of these interesting results will be reported in full in a forthcoming paper.

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The Structure of Fomannosin, a Novel Sesquiterpene Metabolite of the Fungus *Fomes annosus*

Sir:

We wish to report the structure of a biologically active sesquiterpene metabolite of the wood-rotting fungus *Fomes annosus* (Fr.) Karst. This material, which has been named fomannosin (I), has been shown to be toxic toward 2-year-old *Pinus tadea* seedlings, *Chlorella pyrenoidosa*, and some bacteria.[1] The novel ring structure of this unusual sesquiterpene is of special interest since, to our knowledge, this is the first reported example of a sesquiterpene containing the cyclobutene moiety. Although fomannosin follows the isoprene rule, the isoprene units are not connected in the usual head-to-tail sequence.

Fomannosin was isolated by chloroform extraction of a still culture of *Fomes annosus* which was at least 6 weeks old. The chloroform extracts were purified by column chromatography, followed by preparative thin layer chromatography (ptlc), giving the pure toxin as a noncrystalline semisolid. Attempts to crystallize the toxin were unsuccessful. However, the material purified as above was homogeneous by thin layer chromatography in three dissimilar solvent systems. Fomannosin is unstable, and consequently we were unable to obtain a satisfactory elemental analysis. We also found it necessary to use freshly purified material (ptlc) for experimentation and spectral analysis.

Fomannosin ($C_{15}H_{18}O_4$)[2] has $\nu_{max}^{CS_2}$ 3450 (OH), 1745 and 1715 cm^{-1} (C=O) and $\lambda_{max}^{C_2H_5OH}$ 261 mμ (ϵ 9400). The 100-Mc nmr spectrum of fomannosin is shown in Figure 1A.

A dihydro derivative of fomannosin was obtained by catalytic hydrogenation. Dihydrofomannosin (II) ($C_{15}H_{20}O_4$),[3] mp 71–72°, has $\nu_{max}^{CS_2}$ at 1745 and 1720 cm^{-1} and a plateau in the ultraviolet spectrum, $\lambda^{C_2H_5OH}$ 205–217 mμ (ϵ 6230). The 1745-cm^{-1} band in the infrared spectrum of II was attributed to a five-membered-ring nonconjugated ketone on the basis of the following evidence. Dihydrofomannosin formed a 2,4-dinitrophenylhydrazone derivative[3] [mp 220–225°, *m/e* 444.1635 ($C_{21}H_{24}N_4O_7$ requires mass 444.1645] which did not contain the 1745-cm^{-1} band but did have $\nu_{max}^{CS_2}$ 1725 cm^{-1}. The ultraviolet spectrum of the dinitrophenylhydrazone, $\lambda_{max}^{C_2H_5OH}$ 360 (ϵ 2.35 × 10^4), 274 (ϵ 1.15 × 10^4), and 232 mμ (ϵ 2.36 × 10^4), indicated that the ketone with which the 2,4-dinitrophenylhydrazine had reacted was not conjugated.

The assignment of the 1720-cm^{-1} band exhibited by II to a conjugated δ-lactone was based on the following data. Attempts to prepare a bis-2,4-dinitrophenylhydrazone of II were not successful. Allowing II to react with a second mole of hydrogen gave a tetrahydro derivative which had only one carbonyl band in the infrared (1740 cm^{-1}) and no appreciable ultraviolet absorption. Treatment of II with 1 equiv of base at room temperature afforded an acid which gave a noncrystalline ester upon reaction with diazomethane. Dihydrofomannosin could be regenerated from the ester by acid catalysis.

Furthermore, the spectral and hydrogenation data indicated that the chromophore in I was a diene lactone. The more easily reduced double bond must be disubstituted and the double bond α to the lactone must be tetrasubstituted since the two olefinic proton resonances in the nmr spectrum of I are absent in the nmr spectrum of II (Figure 1A, B).

Dihydrofomannosin formed a monoacetate ($C_{17}H_{22}O_5$),[3] $\nu_{max}^{CS_2}$ 1740 cm^{-1}. It was inferred that a primary alcohol had been acetylated since a two-proton singlet at δ = 4.28 ppm in the nmr spectrum of dihydrofomannosin had shifted to δ = 4.78 ppm upon forma-

(1) C. Bassett, R. T. Sherwood, J. A. Kepler, and P. B. Hamilton, submitted for publication.
(2) The molecular formula of fomannosin is inferred from elemental analyses, from high-resolution mass spectra of the dihydro derivatives, and from the integration of its nmr spectrum.
(3) A satisfactory elemental analysis was obtained for this material.

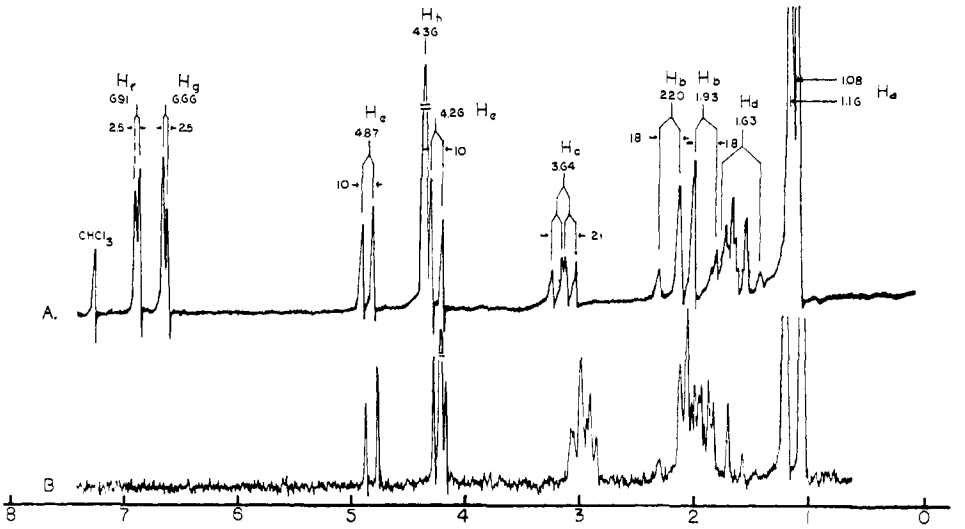


Figure 1. 100-Mc nmr spectra of fomannosin (A) and dihydrofomannosin (B). Chemical shifts are expressed in parts per million from tetramethylsilane and the coupling constants are given in cycles per second. The hydroxyl hydrogen has been exchanged with deuterium oxide to simplify the spectra.

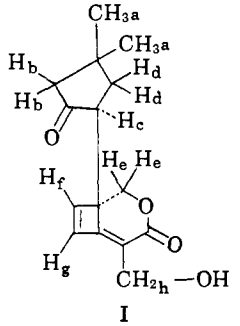
tion of the acetate. The chemical shift of this signal, coupled with its absence in the nmr spectrum of the tetrahydro derivative, suggested that the alcohol was allylic even though attempts to oxidize it with manganese dioxide failed.

The structure of dihydrofomannosin was determined by X-ray crystallographic analysis of its *p*-bromobenzoylurethan derivative ($C_{23}H_{24}BrNO_6$),[3] mp 183–186°.

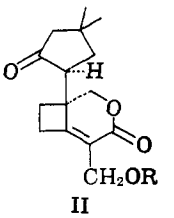
Dihydrofomannosin *p*-bromobenzoylurethan crystallizes in the monoclinic system, space group $P2_1$, with two molecules of $C_{23}H_{24}BrNO_6$ in a cell of dimensions a = 11.57, b = 6.05, c = 15.78 A, β = 95° 35′. Three-dimensional X-ray intensity data were recorded on equiinclination Weissenberg photographs and visually estimated; in all 1610 [F_o] values were obtained.

The initial position of the bromine atom was determined from the three-dimensional Patterson synthesis and the other atoms, apart from hydrogen, were then located by evaluating three-dimensional electron-density distributions with Fourier coefficients weighted according to the method proposed by Sim.[4] The atomic coordinates and temperature factors (anisotropic for the bromine atom, isotropic for the remainder) were then refined by the method of least squares. The present value of R is 11.4%.

The results establish that the *p*-bromobenzoylurethan has structure and relative stereochemistry II (R = $CONHCOC_6H_4$-*p*-Br), and it therefore follows that dihydrofomannosin has structure II (R = H).



I



II

Fomannosin must therefore have structure I since there is only one position to place the missing double bond which satisfies the spectral and chemical data obtained for I. The diene lactone moiety fits well with the ultraviolet and hydrogenation data as previously mentioned. Furthermore, each proton in I can be unequivocally assigned to a signal in the nmr spectrum of fomannosin, as shown in Figure 1A.

The coupling constant (J = 2.5 cps) between H_f and H_g is consistent with a cyclobutene ring[5] and the chemical shifts of H_g and H_f (δ 6.66 and 6.91 ppm) are readily explained by the fact that they are at the end of an extended conjugation system.

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The Thermal *cis–trans* Isomerization of Diimide. A Theoretical Study

Sir:

Recent spectroscopic investigations on the structure of diimide[1,2] have prompted us to study the *cis–trans*

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