be noted that the loss of RR intensity near the band maximum cannot be attributed to more efficient photobleaching in this region because the conditions of the experiments preclude such artifacts[25].) The scattering cross section is also negligible with excitation at 840 nm. This wavelength lies between the P* absorption and the Q_y absorptions of the accessory BChls ($\sim$800 nm). As the excitation wavelength approaches resonance with the Q_y absorptions of these latter pigments, RR scattering is again observed (Figure 2, top trace). The RR bands of the accessory BChls appear as a broad doublet with maxima near 115 and 128 cm^{-1} and a sharper singlet near 188 cm^{-1}. These frequencies are distinctly different from those exhibited by P (102 and 138 cm^{-1}); however, the two highest frequencies are similar to those previously observed in Soret-excitation RR studies of BChl in solution (130 and 198 cm^{-1}).[26]

There are several possible interpretations for the features observed in the low-frequency, near-infrared-excitation RR spectra of the RCs: (1) The 102- and 138-cm^{-1} RR bands of P and the 115-, 128-, and 188-cm^{-1} bands of the accessory BChls are all due to out-of-plane deformations of the BChl macrocycles. The two RR bands of P are due to the same vibrations that give rise to the two lowest frequency bands of the BChls. The frequency differences between the analogous bands of P and the accessory BChls arise because the structures of the BChl molecules in P are different from those of the accessory pigments. (2) The low-frequency RR bands of P and the accessory BChls are all due to out-of-plane deformations of the macrocycles; however, the bands observed for P are not due to the same modes as those observed for the BChls. The different RR intensity enhancement patterns arise because the properties of the P* state are distinctly different from those of a typical Q_y excited state of BChl. (3) The low-frequency RR bands of P are not due to typical out-of-plane deformations of the macrocycles (such as those that give rise to the RR bands of the accessory BChls) but rather to modes that are unique to the dimer. These dimer modes exhibit substantial RR intensity because of the unique properties of the P* state.

Of the three possible interpretations of the RR spectra given above, option 3 is most consistent with all of the data. Option 1 requires that the structures of the BChls in P are quite different from those of the accessory BChls. This requirement is not consistent with Soret-excitation RR studies of RCs.[27,28] These studies indicate that the structures (coordination number, core size, extent of nonplanarity) of the accessory and special pair BChl macrocycles are not significantly different. Both options 1 and 2 require that the low-frequency RR bands of P are due to typical out-of-plane deformations of the BChl macrocycles. The excited-state origin shifts for these modes (as well as the in-plane modes of the macrocycles) are expected to be relatively small.[22,26] Under these conditions (small displacement limit), equal RR intensity is expected with excitation at the electronic system origin and the first vibronic satellite of a given mode.[21] Both the 102- and 138-cm^{-1} RR bands of P exhibit the largest intensity with excitation near 920 nm. This suggests that the system origin is in this vicinity (or somewhat bluer). However, neither mode exhibits an intensity enhancement pattern that is consistent with the small displacement limit. Instead, the diminished RR intensity at higher excitation energies (resonant or near resonant with the first vibronic satellite of either mode) is as expected for relatively large origin shifts along the coordinates of the 102- and 138-cm^{-1} modes. The fact that the intensities of these RR bands (with $\lambda_{ex} = 920$ nm) are similar to those of the low-frequency RR bands of the accessory BChls (with $\lambda_{ex} = 810$ nm) provides additional evidence that the origin shifts of the former modes are large. If the Huang-Rhys factors (S) were small and comparable for these two sets of modes, the RR scattering from P should be at least 100 times weaker than that from the accessory pigments (based

on the relative absorption at 920 versus 810 nm).

The general features of the RR scattering from P are in reasonable accord with the results of second-derivative absorption[12c,e,23] and hole-burning studies[12c-e] on RCs. These optical studies suggest that the system origin of the near-infrared band is to the red of 910 nm and that the band contour is due to transitions to this level and to the first and second vibronic satellites of a mode whose excited-state frequency is in the range 115–145 cm^{-1} and whose S is in the range 1.3–1.5. Because of the large value of S, it has been suggested that this mode is a characteristic vibration of the dimer rather than a typical low-frequency vibration of BChl.[4,12c-e,22] Either the 102- or 138-cm^{-1} RR vibrations could be the ground-state counterpart of this excited-state mode. Two vibronically active low-frequency modes have not been suggested on the basis of the optical studies; however, the RR data indicate that S could be large for both the 102- and 138-cm^{-1} vibrations. The determination of S from the RR intensities of these modes must await the acquisition of detailed excitation profiles at significantly higher signal-to-noise levels. These data should prove valuable for further determining the detailed nature of the P* state and how its characteristics influence the electron-transfer process.

Structure of Preussomerin A: An Unusual New Antifungal Metabolite from the Coprophilous Fungus *Preussia isomera*

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Reports of interspecies competition among coprophilous (dung-colonizing) fungi have led us to investigate such organisms as potential sources of new, naturally occurring antifungal agents.[1–3] During our investigations of the chemistry associated with these competitive effects, we have discovered a unique new antifungal metabolite from cultures of *Preussia isomera* Cain (CBS 415.82). *P. isomera* is an ascomycete that colonizes cattle dung and exhibits antagonistic activity toward other coprophilous fungi in vitro. We report here details of the isolation, identification, and biological activity of this new metabolite, which we have named preussomerin A (**1**).

Analysis of preussomerin A[4] by HREIMS and ^{13}C NMR spectroscopy indicated that it has the molecular formula $C_{20}H_{14}O_7$ (14 unsaturations). The ^{1}H NMR spectrum contained resonances for four oxygenated methine units and seven protons attached to aromatic or vinylic carbons, while the ^{13}C NMR data indicated a total of 14 sp^2-hybridized carbons (Table I). Treatment of preussomerin A with Ac_2O/pyridine afforded a triacetylated product. Two oxygenated methine proton signals at 5.61 and 5.21 ppm were shifted to 6.42 and 6.48 ppm in the acetylation product, indicating that these signals are associated with secondary hydroxyl groups in the natural product. The remaining OH group of preussomerin A is phenolic. Analysis of coupling constants,

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(4) *P. isomera* was grown in liquid shake culture on potato-dextrose broth. Extraction of 4-wk-old liquid cultures with ethyl acetate, fractionation of the extract by silica gel chromatography, and separation of the antifungal fractions by HPLC (C_{18}) afforded preussomerin A: isolated yield, 3–6 mg/L; mp 235–240 °C; $[\alpha]_D$ –212° (c 0.05; MeOH; 31 °C).

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Table I. Proton and Carbon Nuclear Magnetic Resonance Data and Selective INEPT ^{1}H–^{13}C Correlations for Preussomerin A (1)[a]

| C no.	^{1}H	^{13}C	carbons obsd in selective INEPT expts
1	5.61 (br s)	69.2	4,[b] 5, 6,[b] 7,[c] 8,[b] 9, 10
2	3.80 (dd, 4.6, 1.5)	53.2	1, 3, 5,[b] 9,[b] 10
3	3.88 (d, 4.6)	53.1	2, 4, 5, 6,[b] 10[b]
4	–	96.2	
5	–	114.8	
6	–	144.5	
7	6.60 (d, 9.2)	117.3	4,[b] 5, 6, 9
8	6.70 (d, 9.2)	120.3	1,[b] 6, 9, 10
9	–	151.8	
10	–	117.1	
1'	5.28 (br s)	66.0	2', 3', 4',[b] 5', 8',[b] 9', 10'
2'	6.30 (dd, 10.8, 2.9)	125.7	1', 5',[b] 10'
3'	6.63 (d, 10.8)	143.0	4', 10'[b]
4'	–	91.1	
5'	–	117.4	
6'	–	150.2	
7'	6.73 (d, 8.1)	114.6	4',[b] 5', 6', 9', 10'[b]
8'	7.27 (dd, 8.1, 8.1)	130.5	5',[b] 6', 7'
9'	7.36 (d, 8.1)	118.7	1', 5', 6',[b] 7', 8', 10'
10'	–	143.3	

[a] Data were recorded in acetone-d_6 at 360 and 90.7 MHz, respectively. Selective INEPT experiments were individually optimized for 4, 7, 10, or 15 Hz. [b] Denotes a four-bond correlation. [c] Denotes a five-bond correlation.
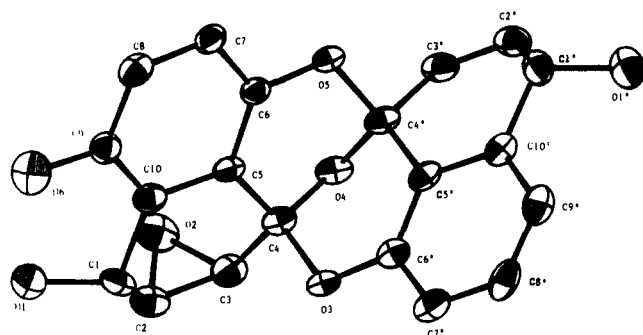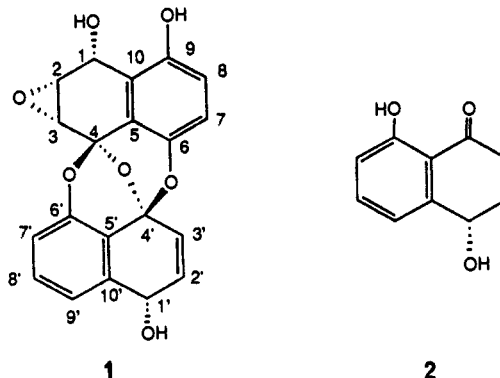

Figure 1. An ORTEP representation of preussomerin A (1), including absolute configuration. Hydrogens are omitted for clarity.

chemical shifts, and decoupling experiments revealed the presence of 1,2,3-trisubstituted and 1,2,3,4-tetrasubstituted aromatic rings, a secondary hydroxyl group adjacent to a cis-disubstituted double bond, and another secondary hydroxyl group adjacent to a 1,2-disubstituted epoxide. The only ^{13}C NMR signals not accounted for by the above units were two singlets (96.0 and 91.1 ppm) consistent with the presence of two ketal carbons. The upfield disposition of these signals relative to those of typical ketal carbons suggested their connection to olefinic or aromatic carbons.[5a,b]

A one-bond heteronuclear C–H shift correlation experiment and a series of selective INEPT[6,7a] experiments (Table I) permitted the establishment of partial structures a and b, although some of the assignments were complicated by observation of an unusually large number of four-bond correlations. In one case, a five-bond correlation was observed.[8] Because there were no long-range NMR correlations between the two subunits a and b, and because two ring unsaturations were not accounted for by the known structural units, the two fused-ring systems must be

a　　　**b**
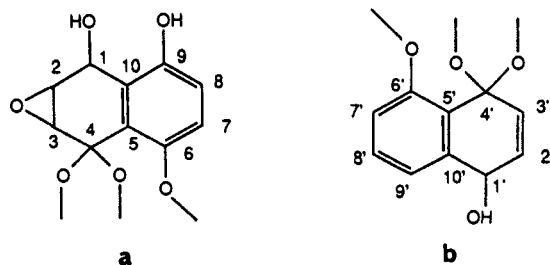
connected through three oxygen atoms in the only reasonable way as shown in **1**. This proposed structure, including relative

1　　　**2**

stereochemistry, was confirmed by X-ray diffraction analysis of a crystal obtained through slow evaporation of a methanol solution of 1.[9] An ORTEP rendering of preussomerin A is provided in Figure 1. This unusual, rigid structure requires that both partially saturated rings adopt boat conformations and places the planes of the two aromatic rings almost exactly perpendicular to each other. The absolute stereochemistry was assigned as shown on the basis of the isolation of (−)-regiolone (**2**) as a decomposition product.[11] The novel polycyclic bis-ketal ring system found in preussomerin A (**1**) has not been previously described.

Preussomerin A displays activity against the early successional coprophilous fungi *Sordaria fimicola* (NRRL 6459) and *Ascobolus furfuraceus* (NRRL 6460), causing a 50% reduction in growth rates at concentrations of 200 and 50 μg/mL, respectively. More detailed studies of the chemistry and biological activities of this compound and related minor components of the *P. isomera* extract will be reported elsewhere.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, interatomic distances, and bond angles for preussomerin A (6 pages). Ordering information is given on any current masthead page.

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(8) Such long-range CH couplings in aromatic systems are typically small but can be 1 Hz or larger[7b,c] and are detectable in selective INEPT experiments.[7a]

(9) Preussomerin A crystallized in the space group $P2_1$ with cell dimensions $a = 11.380$ (2) Å, $b = 9.453$ (2) Å, and $c = 11.551$ (2) Å. The unit cell comprised two molecules of preussomerin A and two molecules of methanol. A half-sphere of diffraction intensity data (3709 total measurements) was collected for 2θ from 2° to 140° (Cu Kα radiation; $k = 1.5418$ Å) with an Enraf-Nonius four-circle automated diffractometer. The 3709 measurements yielded 2743 observed reflections which averaged to 1815 unique reflections (internal agreement = 3.4% on F), of which 1306 had values greater than 3σ. The structure was solved by MULTAN[10] and refined by full-matrix least squares. All H atom positions were found from difference maps, but they were put in ideal fixed positions and not refined. The final refinement, based on 1306 reflections and 261 parameters, gave $R_1 = 0.065$, $R_2 = 0.099$.

(10) Version of MULTAN: Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. University of York, England, 1978, 1980.

(11) The ketal linkages in **1** are somewhat resistant to hydrolysis, but a number of decomposition products were formed upon treatment with acid, most of which were present in very small quantities. The major isolated product was found to be (−)-regiolone (**2**),[12] which resembles partial structure b and could arise via protonation at C-2' during the decomposition process.

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