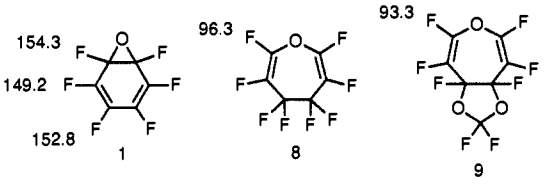
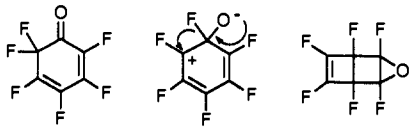


1 8 9

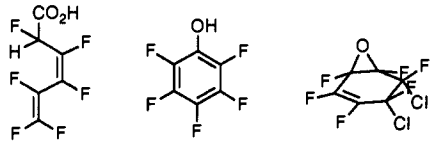
dienone (**10**)[3,10] in acetonitrile or acetone. Warming of solutions in nonpolar solvents gave the same result. These observations are consistent with ring opening of **1** to zwitterion **11** followed by a 1,2-shift of fluoride. Our finding that the reaction is accelerated by Lewis or Brønsted acids lends credence to this pathway. Barlow found that heating hexafluoro Dewar benzene oxide (**12**) in the liquid or gas phase gave dienone **10** as the principal product.[3] Presumably **1** formed as an intermediate in that transformation and rearranged via **11**, as suggested by the authors, or perhaps via the analogous biradical in the case of high-temperature gas-phase pyrolysis.



10 11 12

Irradiation of **1** in the presence of benzophenone at wavelengths >340 nm, to insure excitation only of the triplet sensitizer, yielded again the dienone **10**. Direct photolysis of the benzene oxide gave the unsaturated acid **13**, presumably via **10**. The same acid is formed when **10** is irradiated similarly, via electrocyclic ring opening to a ketene which is hydrolyzed by traces of water in the solvent.[11] Thus, benzene oxide **1** rearranges cleanly to dienone **10** in the ground state and upon excitation into either its S_1 or T_1 state.

Benzene oxide **1** is reduced under very mild conditions to pentafluorophenol (**14**). Sodium iodide in acetone, for example, effects this transformation cleanly at room temperature. The reaction takes place faster than the spontaneous rearrangement to dienone **10** in acetone, and **10** was ruled out as an intermediate by the finding that it yields other products under the reaction conditions. Whether reduction of **1** by iodide ion proceeds via electron transfer or nucleophilic attack is not known. The great susceptibility of the benzene oxide to reduction accounts for the fact that our earlier attempts to synthesize it via reductive dechlorination of **15** gave only **14**.[4]



13 14 15

The behavior of the ^{19}F NMR spectrum of **1** as a function of temperature is striking. At −40 °C in chlorobenzene the spectrum is sharp, with well-resolved spin–spin splitting. All three resonances broaden and then narrow again as the temperature is increased, but the extent of broadening and the temperature where it becomes maximal are different for each signal. *These observations reveal the existence of a dynamic equilibrium between the benzene oxide and a species that is not independently observed, undoubtedly the oxepin* **2**.

On the basis of the spectra of model compounds, the four fluorines distal to oxygen in the oxepin are expected to have chemical shifts in the 140–160 ppm range where the entire spectrum of **1** appears; those geminal to oxygen should appear close to 95 ppm, as noted above. In the intermediate exchange rate regime, therefore, the signal for the fluorines geminal to oxygen in **1** should be much broader than the other two, reach maximum breadth at a higher temperature, and move downfield as the temperature is raised (expectations confirmed by computer simulation). This is precisely the behavior we observe for the highest field resonance of **1**, which broadens more than 10-fold and shifts downfield rapidly as it resharpens above 50 °C. We have not yet been able to detect the oxepin directly, even with high signal-to-noise ratios at temperatures low enough that its spectrum should be sharp. The equilibrium between **1** and **2** clearly lies far on the side of the benzene oxide.

In contrast, the parent benzene oxide–oxepin equilibrium is quite evenly balanced.[12] This fact together with the powerful destabilization of three-membered rings which results from fluorine substitution[13] led us to speculate at the outset of our work that **2** would predominate very heavily over **1**. We regard the gulf between this prediction and the experimental facts as one of the most interesting observations to emerge from our study.

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Near-Infrared-Excitation Resonance Raman Spectra of the Primary Electron Donor in Photosynthetic Reaction Centers from *Rhodobacter sphaeroides*

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The X-ray crystal structures of bacterial photosynthetic reaction centers (RCs)[1-3] serve as bench marks for establishing a detailed description of the light-induced electron-transfer process.[4,5] Much recent work has focused on the characterization of the electronic properties of the primary electron donor state (P*), which is an

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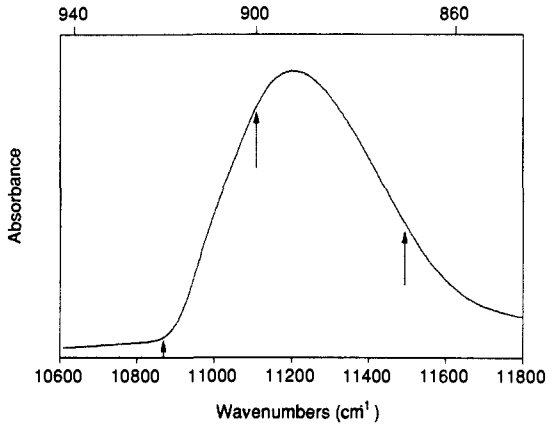

Figure 1. Absorption spectrum of the P* state of RCs from *Rb. sphaeroides*. The spectrum was acquired at 4.2 K in a glycerol glass. The arrows denote several of the excitation wavelengths (920, 900, and 870 nm) used in the RR experiments.

excited state of the special pair dimer of bacteriochlorophyll (BChl) molecules in RCs.[4-20] The characteristic absorption band for this state occurs at unusually low energy (10000–12000 cm^{-1})[6,7] and exhibits distinctive hole-burned[10-12] and Stark effect[14-16] spectra. These properties of P* have been analyzed in attempts to explain both the directionality and mechanism of the initial electron-transfer reaction.[7,9,13,17-20]

Thus far, most studies of P* have relied on optical spectroscopic techniques. No resonance Raman (RR) experiments have been reported that directly probe this state. RR spectroscopy has the potential for providing valuable information concerning the nature of P* because the modes that gain intensity enhancement in the RR spectrum are those that exhibit the largest vibronic activity.[21] Such modes, particularly those in the low-frequency regime, are thought to play a key role in the electron-transfer process.[4,7,22] In this regard, second-derivative[12c,e,23] and hole-burning[12c-e] studies on P* suggest vibronically active modes in the 100–150-cm^{-1} regime. In this communication, we report the results of preliminary, low-frequency RR studies that probe the photophysically important, near-infrared absorption band of the primary electron donor in RCs from *Rhodobacter sphaeroides* wild-type strain 2.4.1.

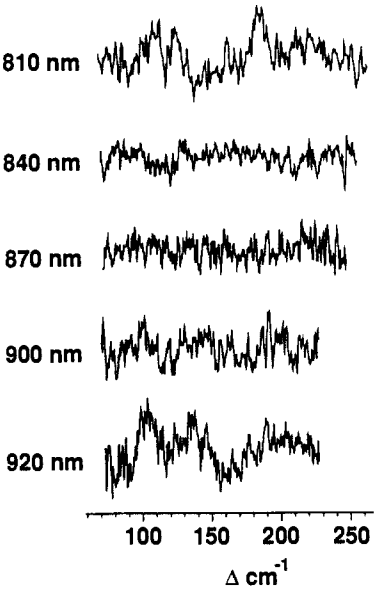

Figure 2. Low-frequency regions of the near-infrared-excitation RR spectra of RCs from *Rb. sphaeroides*. The spectra were acquired at 12 K in a glycerol glass.

The low-temperature (4.2 K) absorption spectrum of the P* state of RCs from *Rb. sphaeroides*[24] is shown in Figure 1. The arrows indicate several of the excitation wavelengths (920, 900, and 870 nm) used in the RR experiments. The low-frequency regions of the RR spectra[25] obtained with excitation at these and several other wavelengths are shown in Figure 2. Although the signal-to-noise ratios are modest, even with the extended data acquisition times used in the experiments (~5 h), RR bands are clearly evident (and reproducible) in certain of the spectra. The most intense RR scattering is observed when the excitation wavelength lies at the extreme red edge of the absorption band near 920 nm. At this excitation wavelength, broad RR bands are discernible near 102 and 138 cm^{-1}. As the excitation is tuned to shorter wavelengths that approach the absorption maximum, the intensities of these RR bands decrease. The RR scattering is sufficiently weak with excitation at 870 nm that no bands are apparent in the low-frequency region of the spectrum. (It should

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(25) The RR spectra were obtained via backscattering from glassed samples (1:1 in glycerol, total concentration 45 μM) at ~12 K. Temperature control was achieved by mounting the samples, contained in capillary tubes, via a home-built holder onto the cold tip of a closed-cycle refrigeration system (ADP Cryogenics DE-202 Displex). The spectra were acquired on a triple-stage spectrometer (Spex Industries 1877D) with silvered optics and 1200 groove/mm holographic gratings optimized for response at 900 nm in both the filter and spectrograph stages. A computer-controlled (Macintosh II) charge-coupled device (Photometrics PM 512 grade Prime CCD with a series 200 controller) served as the detector. The excitation wavelengths (λ_{ex} = 920, 900, 870, 840, and 810 nm) were provided by the spatially filtered output of a Ti:sapphire laser (Spectra Physics 3900) pumped by an argon ion laser (Spectra Physics 2040). The incident beam was defocused such that the power on the illuminated volume (~1 μL) was 2 mW or less. The resulting photon flux of ~50 photons/s per RC is sufficiently low that less than 1% of the chemically reduced RCs exist in the photogenerated transient states P^+ and ^3P at any of the excitation wavelengths used in the RR experiments. The spectral resolution of the RR experiments was ~1 cm^{-1}. A typical data acquisition consisted of 100 3-min integrations. Cosmic noise spikes were removed via statistical analysis of the data at each pixel. Sample fluorescence was removed via a polynomial fit to the spectrum after a flat field correction. Frequency calibration was accomplished with Xe and Ar lamps.

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 (~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 λ_{ex} = 920 nm) are similar to those of the low-frequency RR bands of the accessory BChls (with λ_{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.

Acknowledgment. This work was supported by Grant GM-39781 (D.F.B.) and GM-30353 (H.A.F.) from the National Institute of General Medical Sciences and by Grant 88-37130-3938 from the Competitive Research Office of the U.S. Department of Agriculture (H.A.F.). We thank Professors D. Holten, R. Friesner, G. Small, and S. Boxer for helpful discussions.

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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 ^1H 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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