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ON THE MOLECULAR STRUCTURE OF BACTERIOCHLOROPHYLL *b*

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(Received

Abstract--The molecular structure of bacteriochlorophyll *b*, isolated from *Rhodopseudomonas viridis*, is proposed on the basis of measurements of its infrared, mass and proton magnetic resonance spectra. The proposed structure differs from that of the known molecule, bacteriochlorophyll *a*, in the absence of two hydrogen atoms from carbon atoms C-4 and C-4' of the substituent of ring II of the porphyrin. Apart from possible stereochemical differences, bacteriochlorophyll *b* may therefore be designated as 4-desethyl-4-ethylidenebacteriochlorophyll *a*. The known electronic spectral properties and chemical instability of the bacteriochlorophyll *b* pigment are explained in terms of the proposed structure, and the evolutionary significance of its relationship to bacteriochlorophyll *a* is discussed.

Abbreviations: BChl, bacteriochlorophyll; Chl, chlorophyll; PMR, proton magnetic resonance.

A pigment resembling bacteriochlorophyll in its optical properties was obtained from a photosynthetic bacterium newly isolated by Eimhjellen, et al.[1a] and subsequently named Rhodopseudomonas viridis.[1b] This pigment nevertheless clearly differed from the normal bacteriochlorophyll molecule in its spectral and chromatographic properties and was named bacteriochlorophyll b. The pigment is of special interest because its long wavelength absorption band in vitro occurs at the lowest energy of any known chlorophyll, and in vivo it is able to utilize low energy photons of 1030 nm wavelength in order to carry out photosynthesis efficiently.

In a preliminary report of the properties of bacteriochlorophyll b and of its oxidation products, Brockmann and Kleber[2] proposed a tentative structure which was essentially an epimer of bacteriochlorophyll a at carbon atom C-3 or C-4. We present evidence from PMR spectroscopy which is inconsistent with that proposed structure and which, together with infrared and mass spectra, supports the structure 2-desethyl-2-ethylidenebacteriochlorophyll a. The structure proposed is, therefore, tautomeric with a chlorophyll, rather than with bacteriochlorophyll a, and this may help to account for its ready "oxidation" to a compound with the chlorin spectrum.

RESULTS

Absorption and Circular Dichroism Spectra

The absorption spectrum of BChl b in acetone solution is shown in Fig. 1. The wavelengths of the absorption maxima agree closely with those reported by Eimhjellen et al.;[1] however, the small peak at 670 nm in their spectrum (attributed to oxidized BChl b) is absent in our spectrum. Absorbance ratios, calculated relative to the long wavelength peak at 794 nm, are compared in Table 1 with two sets of values

reported previously. Minimum values of the relative absorbances at 680, 582, 530 and 450 nm are considered to be important criteria of purity.

The circular dichroism spectrum measured in ether solution showed no measurable peaks either at 794 or at 582 nm. An upper limit for the magnitude of the molar circular dichroism is $|\Delta\varepsilon| < 2$ ℓ-mole^{-1}-cm^{-1}.

Infrared Spectrum

The infrared spectra of BChl a and BChl b in tetrahydrofuran resemble one another rather closely. This is particularly true in the carbonyl stretching region[4] (1750-1600 cm^{-1}) shown in Fig. 2. On the basis of the positions and relative intensities of the bands observed at 1735, 1685 and 1655 for BChl a and at 1736, 1689 and 1656 cm^{-1} for BChl b, we conclude that BChl b contains two ester carbonyls, a cyclic ketone in an intact ring V and an acetyl substituent, probably at position C-2. Other major features at lower frequencies to 675 cm^{-1} occur in both spectra.* The most distinctive features of the BChl b spectrum is a pronounced, sharp band at 948 cm^{-1} that corresponds to a relatively weaker peak at 943 cm^{-1} in BChl a. The latter compound exhibits a sharp, relatively weak component at 753 cm^{-1} that is absent in BChl b.

Mass Spectrum

Mass spectra of naturally-occurring chlorophylls or their pheophytins are generally not available in the literature. Dougherty et al.[6] have published an extensive study of a variety of porphyrins, including the methyl esters of pheophorbides a and b.

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*Complete infrared spectra of both BChl a and BChl b are given in ref. 5.

We have obtained mass spectra at low resolution of BChl a, BChl b and their pheophytins. As in the case of chlorophyll c, the parent peak is not observed and the compounds apparently readily lose the phytol esterifying group as well as Mg (where present initially). The mass spectra of BChl a and BChl b resemble one another closely. The peaks of largest mass occur at m/e 627, 625 and 623 (compare with M.W. 624 for methyl bacteriopheophorbide a). The most intense peak for both compounds is m/e 566, representing the loss of $CO_2CH_3 \pm 2H$. Additional prominent fragments can be explained by assuming the loss of $CH_5O \pm 2H$, $CH_2CH_2CO_2CH_3 + 4H$ and $CH_2CH_2CO_2CH_2 + CO_2CH_3 \pm 2H$. Generally similar fragmentation patterns were reported previously for the most closely analogous compounds.[7,8] The mass spectra of the two bacteriopheophytins did not resemble one another so closely and the fragmentation patterns proved impossible to interpret.[5]

In the low mass region all of the compounds (except BChl a) exhibited very large peaks at m/e 278. For BChl a, a similar large peak occurred at m/e 279 for one sample and 274 for another. We cannot account for this discrepancy, as the high mass regions were generally similar for the two samples of BChl a. The m/e 278 peak is attributed to phytadiene, which is the characteristic cleavage product of a phytol ester.[9]

We conclude from the mass spectra that BChl a and BChl b have similar if not identical carbon skeletons and differ at most by two hydrogen atoms. BChl b appears to be esterified by phytol.

Phytol Identification

Phytol can be removed from chlorophylls by dissolution in 2.5% KOH in methanol followed by heating for 20 min at 66°C.[10] The phytol can be

recovered by extraction into ether. The tetrahydroporphin ring of BChl b was oxidized by this procedure, and the products other than phytol were not recovered.

The procedure of Shimizu, et al.[11] was used for the identification of phytol. The compound obtained from BChl b cochromatographed with authentic phytol on silica gel thin-layer sheets (Eastman Chromagram Sheet K301R) in two different solvent systems: benzene/ethyl acetate (19/1) and isooctane/ethyl acetate (85/15).

PMR Spectra

The best diagnostic method for characterizing individual chlorophylls is high resolution PMR spectrometry. We have recorded spectra at 220 MHz of several samples of BChl b and BChl a in d_6-acetone and in d-chloroform plus d_5-pyridine. Katz et al. have published numerous articles on the interpretation of the PMR spectra of chlorophylls and related compounds,[4,12] including methyl bacteriopheophorbide a. The PMR spectrum of BChl a was reported and partially assigned by Sauer et al.[13] and by Dougherty et al.,[14] as was that of its oxidation product by Lindsay Smith and Calvin.[15] Because of the similarities and the significant differences between the PMR spectra of BChl a and BChl b, we will interpret the observations on the latter compound in the light of the assignments for the former.

For the purposes of PMR spectrometry it was necessary to prepare relatively large (20 mg) samples of BChl b of high purity. Problems were encountered because of the great instability of the pigment in light and in the presence of small amounts of oxygen. Early preparations gave evidence of a number of variable or otherwise clearly

spurious peaks. Most of these were eliminated from the final samples to be reported here, although there was some evidence of possible conversion after several days of successive measurements and transfer to different solvents. Double resonance (proton decoupling) experiments add essential information for the resolution of the unique aspects of the BChl b structure. Although measurements were made at both 60 and 220 MHz, the numerical data reported here refer only to measurements at the higher frequency.

The PMR spectra of BChl b in two solvent systems, d_6-acetone and d-chloroform plus d_5-pyridine, are shown in Figs. 3 and 4. A comparison with the chemical shifts for BChl a in d_6-acetone, for phytol in d-chloroform and our proposed assignments are included with the data on BChl b in Table 2. A cursory inspection of the PMR spectra of the two bacteriochlorophylls in d_6-acetone shows the presence of substantial qualitative differences--much greater than were observed in the infrared or mass spectra. Initial analyses showed that much of this dissimilarity results from a strong shift to lower field of the major phytyl resonances in BChl a relative to BChl b. In this respect BChl a (along with its oxidation product, 3,4-dehydroBChl a[15]) is the compound that is unusual, as the chemical shifts of the phytyl protons in BChl b closely match those of Chl a, Chl b and their pheo-phytins[12] as well as those of purified phytol in d-chloroform.[16] This is an unexpected and unprecedented feature, which had gone unnoticed previously in this laboratory[13,15] and for which we find no ready explanation on the basis of the known structural properties of BChl a a. Although its investigation is outside the scope

of the present study, it clearly presents a challenge to future investigators in this area.

Beginning with the low field region, Table 2 and Figs. 3 and 4 indicate the presence of three single proton peaks in BChl b in the region (8-9 ppm) characteristic of methine bridge protons. In this respect the compound resembles all other known chlorophylls except those from Chlorobium, which have meso alkyl substituents at the methine bridge positions.[17] Of the three methine proton resonances in BChl b, those at highest and lowest field are close to resonances of BChl a, whereas the third peak occurs in the low field region in BChl a and in the high field region in BChl b. We shall explain this in terms of a perturbation of the π-electron distribution in the vicinity of one of the methine protons.

The single proton resonance near 6 ppm is readily assigned to the C-10 proton of ring V. It is noteworthy only in that there is no evidence in any of our spectra in d_6-acetone of a satellite peak that might result from epimerization at this asymmetric center; however, in d-chloroform plus d_5-pyridine a small satellite peak of about 1/3 the area is observed at 0.127 ppm to higher field. This difference in chemical shift is just what one expects for the epimer at C-10.[18]

Passing over the region from 4 to 6 ppm for the moment, we find four narrow peaks in the region from 3 to 4 ppm. Each of these integrates to about three protons, although a number of much smaller peaks are also apparent in the spectra. By analogy with other chlorophyll assignments,[4] we attribute the major resonances to four isolated methyl groups at positions C-11, C-5, C-1 and C-2 (acetyl).

The high field region of BChl b is dominated by the very large peaks at 0.85 and 1.30 ppm resulting primarily from the methyl and methylene protons of the phytyl group. The presence of these large peaks prevents the observation of any underlying peaks which may be associated with the porphyrin substituents. The singlet peak (3 protons) near 1.6 ppm is assigned to the isolated methyl substituent of the double bond of phytyl. The remaining phytyl protons are expected to occur near 2.0 ppm (2 protons-triplets), 4.2 ppm (2 protons-doublets) and 5.1 ppm (1 proton-triplet). None of these regions is clear of other resonances (see below) and the assignments cannot be confirmed. For technical reasons it proved impossible to apply the double resonance approach to verify the locations of these particular protons. Each is expected to couple to one or more protons within 1 ppm in its vicinity.

The region between 1.4 and 2.4 ppm contains four resonances that appear to be doublets, in addition to the singlet at about 1.6 ppm already assigned to phytyl. Careful measurements using field scale-expanded traces indicate that each of the splittings is 6-7 Hz. For the two doublets to higher field, double resonance experiments were successful in determining the location of the resonance of the coupled proton. The doublet at 1.64 ppm in d_6-acetone (1.51 ppm in d-chloroform/ d_5-pyridine) is coupled to a proton 591 Hz (593 Hz) downfield at 4.33 ppm (4.20 ppm). The doublet at 1.80 ppm (1.84 ppm) is coupled to a proton 741 Hz (737 Hz) downfield at 5.18 ppm (5.19 ppm). Each of these downfield regions is expected to be the location of resonances of phytyl protons as well. (These phytyl protons should couple among themselves rather

than to anything in the upfield region, however.) The phytyl and porphyrin protons in the 5.1 ppm region are best resolved in d_6-acetone solvent, where two distinct, broad resonances can be seen. In the 4.2-4.3 ppm region all that can be said is that the coupling does not appear to correspond to the center of the broad resonance and the area corresponds to more than one proton. For each of the coupled upfield doublets, the area corresponds to about three protons. Katz et al.[4] have characterized the coupling of the ring protons and methyl protons at C-8 in a variety of chlorins and bacteriochlorin and at C-3 in bacteriochlorin with chemical shift differences of 2.49 to 2.70 ppm. The doublet at 1.63 ppm in d_6-acetone, which is coupled to a proton 2.70 ppm downfield, appears to satisfy this criterion. The doublet at 1.80 ppm is coupled to a proton 3.38 ppm downfield and, therefore, falls well outside the characteristic range. For reasons that will become clear below, we assign the high field doublet to the C-8 methyl substituent and the second doublet to a feature which is unique to BChl b.

Assuming that the phytyl ester is attached to the porphyrin ring via a propionate substituent (as in all known chlorophylls except chlorophyll c, where dehydropropionate appears to be involved[19]), resonance corresponding to four protons is expected at about 2.3 ppm. This should be a complex region, because two of the protons are split by two, and the other two are split both by one and by two protons. The observed multiplet resonance, which appears to be a doublet in d-chloroform/d_5-pyridine, has a more complex shape in d_6-acetone. This solvent effect, which does not occur for the higher field doublets, is taken as evidence that the

doublet at 2.3 ppm in d-chloroform/d_5-pyridine is only apparent. The single C-8 proton is expected to give a resonance near the C-7 proton at 4.3 ppm. Searches for coupling to the C-7' protons by double resonance were unsuccessful, however. Perhaps this was because of the complex nature of the upfield component. A further complication results from the fact that the resonance at 2.3 ppm integrates to about six protons, rather than the four expected. This must be considered to be one of the weaker points in the PMR assignment.

The remaining "doublet" at 1.96 ppm is even less clear-cut. It appears only in the d-chloroform/d_5-pyridine spectrum, as the peak is obscured by the very large peak from residual solvent protons in d_6-acetone. In the former solvent it is not a symmetric doublet and never appeared to be so well resolved as the ones to higher field. Integration is difficult because of a rising "background" in this region, but it appears to correspond to four to five protons. As noted above, the two protons (each coupled to two protons) of the methylene adjacent to the double bond in phytyl is expected to occur in this region. Searches for coupling with downfield protons were unsuccessful, but the poorly resolved band-shape presented problems of recognition. This feature is also thought to reflect, at least in part, a unique element of the BChl b structure.

Apart from specifying the features unique to BChl b, this completes the assignment of the PMR spectrum, including the features previously by-passed in the region from 4 to 6 ppm. The latter have been assigned by means of coupling to upfield doublets or to phytyl resonances.

Nevertheless, we hasten to agree with the observant reader who notes that we have so far ignored three rather prominent features exhibited in Figs. 3 and 4. A large resonance, apparently triplet, appears at 1.095 ppm in Fig. 3. This feature was found to be quite variable from sample to sample, and in one spectrum in d_6-acetone it was observed to be totally absent. In the spectrum of Fig. 4 it is at most an ill-defined shoulder on the phytyl peak at 1.3 ppm. The small, but distinct peak at 7.13 ppm in d_6-acetone (7.07 ppm, multiplet, in d-chloroform/d_5-pyridine) was absent in an earlier preparation and is attributed to an impurity. The quite-prominent apparent doublet at 4.5 ppm in d-chloroform/d_5-pyridine is totally absent in the spectra in d_6-acetone. It is probably significant that the sample studied in the former solvent had been transferred from the latter, had undergone several days of measurements and may have been partially oxidized. On the other hand, no other new peaks attributable to such decomposition products appeared in the downfield region.

THE STRUCTURE OF BACTERIOCHLOROPHYLL b

From the data presented above one can readily support the proposal that BChl b resembles BChl a in all respects except features associated with ring II. The structural feature that is most consistent with the available data was first proposed by A. S. Holt.[20] It proposes the presence of an ethylidene substituent at carbon C-4 in place of ethyl. The difference between BChl a and BChl b is therefore a matter of only two hydrogen atoms, one from C-4 and one from C-4', which are removed in BChl b. The evidence that supports this structure, shown in Fig. 5, can be summarized as follows:

1) The electronic spectrum is expected to be altered because the C-4,4' double bond is adjacent to the porphyrin π-electron system.

2) The proposed structure is tautomeric with a chlorin: a simple shift of the C-3 hydrogen to the C-4' carbon will convert the molecule to 2-desvinyl-2-acetyl chlorophyll a, which is green and has a long wavelength absorption at 677 nm.[15] This may account for the marked instability of BChl b toward chlorin formation, even when oxygen is excluded. It also accounts for the report that BChl a and BChl b (at least their pheophytins) are converted to the same product upon "oxidation".[2]

3) The infrared spectrum of the proposed molecule should be virtually indistinguishable from that of BChl a. The ethylidene function is expected to contribute a weak band near 900 cm^{-1}, and this may be the source of the differences actually observed in that region.

4) The molecular weights appear to differ by at most 2 daltons and, in general, the mass spectral fragmentation patterns are expected to be rather similar, as observed.

5) The PMR spectrum exhibits a resonance involving three protons (at 1.80 ppm in d_6-acetone) coupled to one proton 3.38 ppm downfield. The methyl group and the single proton substituted at the C-4' carbon in the proposed ethylidene would account nicely for the observed peak areas and the coupling. Furthermore, the position of the single proton downfield at 4.3 ppm is consistent with the fact that it is bonded directly to a carbon involved in a double bond, as with the similarly placed proton of phytyl at 5.18 ppm. The absolute chemical shifts cannot be directly compared, however, because of the large additional

contribution from the porphyrin ring current field.

Secondary effects in the PMR spectrum can also be interpreted using the proposed structure. The methyl substituent at C-3 is shifted 0.45 ppm downfield from the nearly equivalent C-8 methyl. Both the adjacent ethylidene double bond at C-4 and ring-strain of pyrrole ring II introduced by this exo-double bond can be expected to effect the PMR of the C-3 methyl. The ring strain may serve primarily to shift the C-3 methyl to a new position in the porphyrin ring current field. In addition, the β methine proton may feel the effect of the ethylidene at C-4 position. This would account for the fact that one of the methine protons is shifted downfield by 0.5 ppm relative to that in BChl a.

The alternative structure proposed by Brockmann and Kleber,[2] which involves a simple epimerization at carbon C-3 or C-4 and, perhaps, a replacement of the C-3 and C-4 protons by other substituents, is not consistent with our evidence. In particular, an ethyl group at C-4 would not account for the three-proton doublet at 1.8 ppm coupled to a single proton rather far downfield. In fact, Inhoffen et al. report that the cis-trans effect on the PMR spectrum of dihydrooctaethylporphin is very small and in the opposite direction.[21] The mass spectrum argues against any replacement of the C-3 and C-4 hydrogens without compensating deletions.

In conclusion, we feel that the proposed structure, which can be designated as 4-desethyl-4-ethylidenebacteriochlorophyll a, satisfies all of the criteria that need to be met in order to explain the physical

properties. Apart from the spurious peaks in the PMR spectra, which we have discussed above, perhaps the principal disconcerting observation is the unusual location of the PMR resonances attributable to phytyl in BChl a. This is certainly a baffling observation and will merit further investigation.

Although the structure has been proposed almost entirely on the basis of measurements made on the native pigment as it is obtained by direct extraction from the intact bacteria, we hoped to provide confirmation of the structure through controlled chemical modification. Clearly, reduction of the ethylidene at C-4 would convert the molecule to BChl a, or to a near analog if the similarly substituted double bond in the phytyl group is also reduced. We attempted to carry out hydrogenation over palladium on carbon in dioxane as solvent. No shift in the electronic absorption spectral bands was observed after 1 hr at 1 atm of H_2. In a control experiment using Chl a under the same conditions, nearly one mole of H_2 was taken up per mole of Chl a, and the long wavelength absorption band shifted from 667 to 650 nm. This presumably resulted from the reduction of the vinyl substituent at C-2 of Chl a. Addition of PtO_2 and exposure of the BChl b solution to 3 atm of H_2 similarly caused no observable change. Increasing the polarity of the solvent by addition of an equal volume of ethanol produced a completely altered electonic spectrum with a long wavelength absorption maximum at 610 nm. The molecular change accounting for this dramatic spectral change was not further investigated; it may have involved the opening of ring V in the presence of ethanol. It may in the future be possible to find conditions which will effect the desired reduction in a controlled fashion. Until that time, however, the results of this approach will remain inconclusive.

CONCLUSIONS

On the basis of evidence from PMR, mass spectra and infrared spectra, the structure of BChl *b* is proposed. It is thought to differ from that of BChl *a* by only two protons removed from the C-4 to C-4' bond. The absolute configuration of the molecule at carbons C-3, C-7, C-8 and C-10 is unknown, but chromatographic identities of oxidation products of the two bacteriochlorophylls[2] suggests that they are identically substituted except, perhaps, at C-3.

The close structural relationship is satisfying from an evolutionary point of view. Assuming that the more widely proliferated organisms containing BChl *a* are indicative of an earlier evolutionary origin, then a mutation which resulted in dehydrogenation of the C-4 to C-4' bond would confer an advantage upon the resulting organism. The concomitant shift in the near infrared absorption band to longer wavelengths would enable the modified organism to utilize light in a region of the spectrum not masked by "normal" photosynthetic bacteria. The presence of such dehydrogenation steps in the later stages of chlorophyll synthesis is well known,[22] although they result in the formation of vinyl substituents (at C-4 and/or C-2) in all other pigments whose structures have been determined. The only analogous compounds with exo-double bond substituents have been observed as products of the photooxidation of protoporphyrin-IX.[23] It will be of interest to learn the biosynthetic pathway by which BChl *b* is produced in the bacteria.

EXPERIMENTAL

Rhodopseudomonas viridis (NHTC 133, obtained from Dr. G. Cohen-Bazire, Dept. of Bacteriology, University of California, Berkeley) was grown in 11.5 liter bottles in the medium described by Eimhjellen *et al.*[1] Illumination was provided by fluorescent lights. Ten-day old cultures were harvested by centrifugation and subjected to the following procedure, carried out in dim green light and under nitrogen: add to the paste 7 parts of acetone and 1 part of water, blend for 3 min, let stand for 30 min, filter through paper, add 5% more water to filtrate and filter through fine sintered glass. The bacteriochlorophyll in the extract is then transferred to isooctane, washed twice with water, dried over Na_2SO_4, concentrated to 150 ml and chromatographed on a powdered sugar column. When the isooctane eluate becomes colorless, indicating removal of most of the carotenoids, the bacteriochlorophyll is eluted using 0.5% n-propanol: isooctane. The leading and trailing portions of the band are discarded, the middle portions washed with cold water to remove the n-propanol, and the solid which appears upon standing is collected by centrifugation. The pigment is stored as the solid under isooctane in darkness at -20°C until needed. Yield: 40 mg BChl *b* from 11.5 liters of bacterial culture.

BChl *a*, obtained from *Rhodospirillum rubrum*, was isolated as described previously.[13] Phytol (K & K Laboratories, Jamaica, N. Y.) was used without further purification.

Visible and near infrared absorption spectra were measured using a Cary Model 14R spectrophotometer, infrared spectra using a Beckman IR-7, circular dichroism spectra using a Durrum-JASCO J-20 spectrometer with long wavelength extension, mass spectra using an AEI Model MS12 instrument

and proton magnetic resonance spectra using a Varian 220 MHz or a Varian A-60 instrument. Chemical shifts were measured relative to TMS as an internal standard. Integration of the peak areas was carried out graphically on the PMR absorption traces.

Solvents were reagent or spectral grade. d_6-Acetone (>99.5 d) and d_5-pyridine (>98% d) were obtained from Volk (Burbank, Calif.) and d-chloroform (>99.8% d) from Bio-Rad (Richmond, Calif.).

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TABLE 1. BACTERIOCHLOROPHYLL B ABSORBANCE RATIOS

(Solutions in Acetone)

Reference	$\frac{A_{\lambda}}{A_{794}}$	$\frac{A_{680}}{A_{794}}$	$\frac{A_{582}}{A_{794}}$	$\frac{A_{530}}{A_{794}}$	$\frac{A_{450}}{A_{794}}$	$\frac{A_{407}}{A_{794}}$	$\frac{A_{368}}{A_{794}}$
Eimhjellen et al.[1]	*	0.19	0.31	--	0.315	0.86	0.84
Jensen et al.[3]		0.16	0.31	--	--	0.90	1.04
This study		0.094	0.27	0.036	0.15	0.823	0.94

*Ratios estimated from the spectrum shown as Fig. 1 of the reference.

Ratios recalculated from values based on the peak at 368 nm.

TABLE 2. PROTON MAGNETIC RESONANCE AT 220 MHz

OF BACTERIOCHLOROPHYLLS A AND B AT 18°C

	Chemical Shift, δ, ppm			
	BChl a in d_6-acetone	BChl b in d_6-acetone	Bchl b in d-chloroform plus 15% d_5-pyridine	Phytol in d-chloroform
α	8.80	8.90 or 8.88	9.07 or 8.89	
β	8.38 or 8.36			
δ		8.41	8.26	
10	5.88	5.85	6.20	
(10') epi	--	--	(6.08)	
4!	--	5.18	5.19	
Phytyl $-O-CH_2-C(H)=$	?	5.08	5.24	5.45
Phytyl $-O-CH_2-C=$	?	4.30	4.20	4.15
8	4.34 (?)	4.33	4.20	
11	3.75	3.75	3.85	
5 and 1	3.39 3.26	3.40 3.30	3.54 3.51	
2	2.97	3.00	3.16	
7' and 7"	2.40,2.49	2.30	2.28,2.31	
Phytyl $=C(CH_2-)-$	? (Acetone)	(Acetone)	?	2.03
3'				1.96
4"	--	1.80	1.84	
Phytyl $=C(CH_3)-$	(Acetone ?)	1.56	1.65	1.68
8'	1.69 (?)	1.64	1.51	
Phytyl	1.93 1.54	1.29 0.84	1.30 0.88	1.22 0.92,0.82
4"	1.08	--	--	

FIGURE CAPTIONS

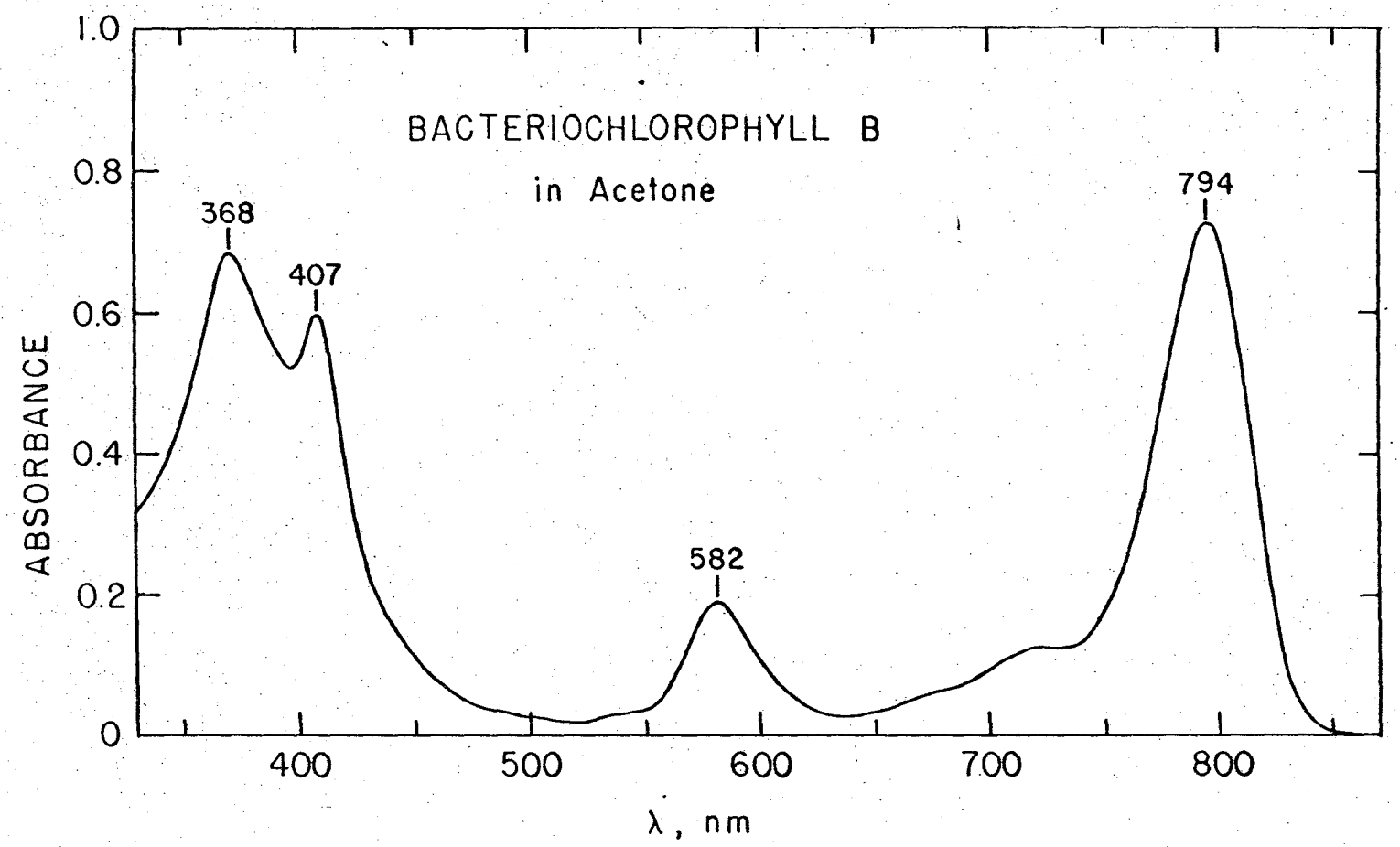
Fig. 1. Absorption spectrum of bacteriochlorophyll b in acetone solution from 330 to 870 nm; path length 1 cm.

Fig. 2. Infrared spectrum of bacteriochlorophylls a and b in tetrahydrofuran solution from 1600 to 1750 cm^{-1}.

Fig. 3. Proton magnetic resonance spectrum of bacteriochlorophyll b in d_6-acetone at 220 MHz and 18°C.

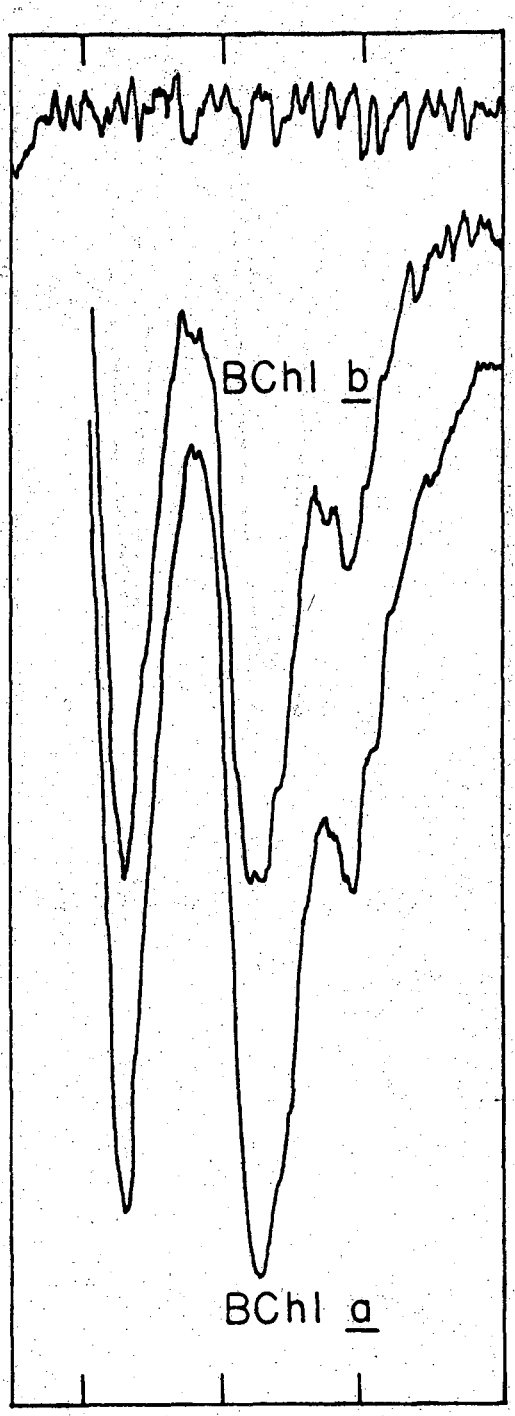
Fig. 4. Proton magnetic resonance spectrum of bacteriochlorophyll b in d-chloroform + d_5-pyridine (~15%) at 220 MHz and 18°C.

Fig. 5. Proposed molecular structure of bacteriochlorophyll b.



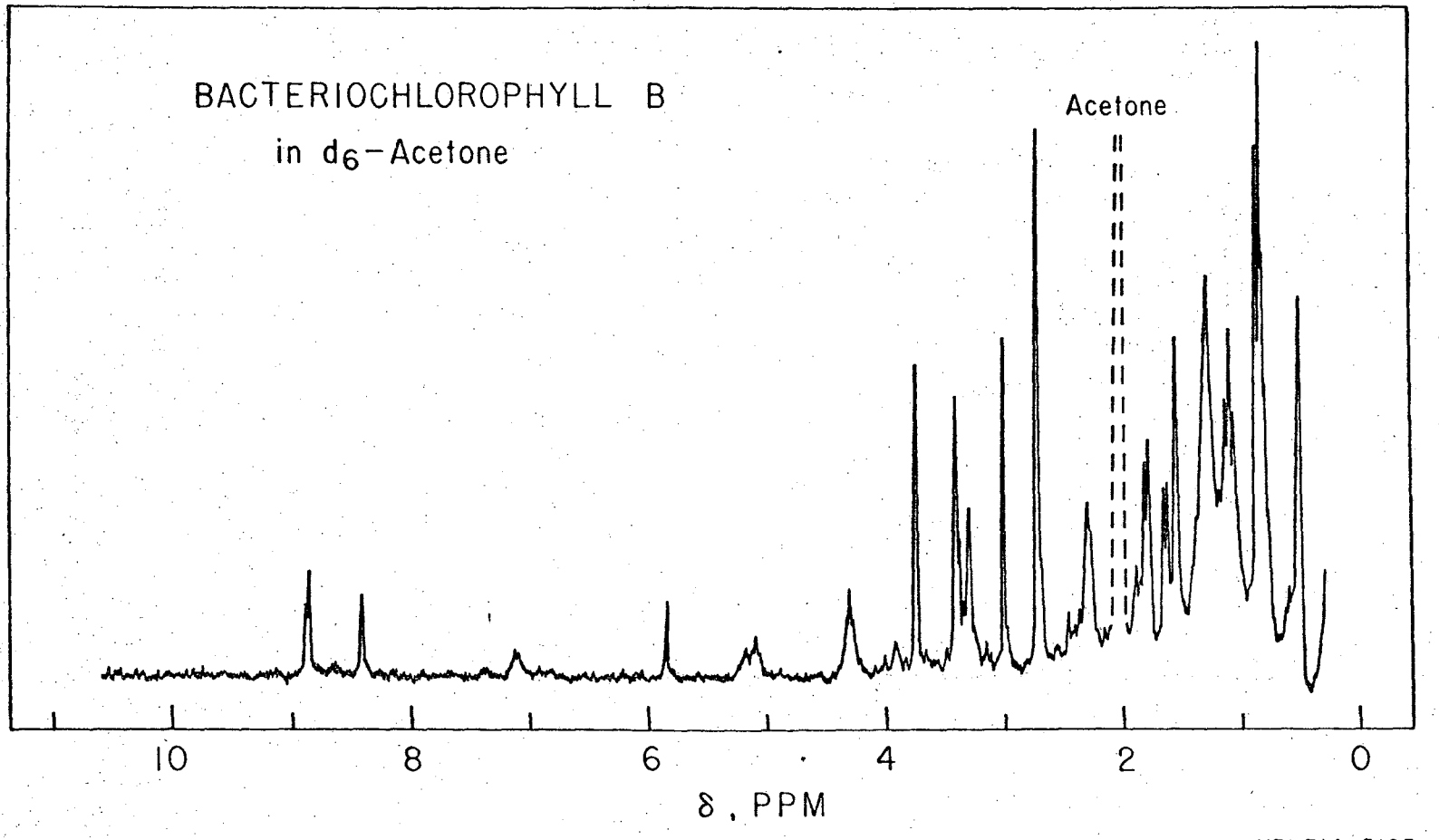
XBL714-5106

Sauer & Baumgarten
Fig. 1



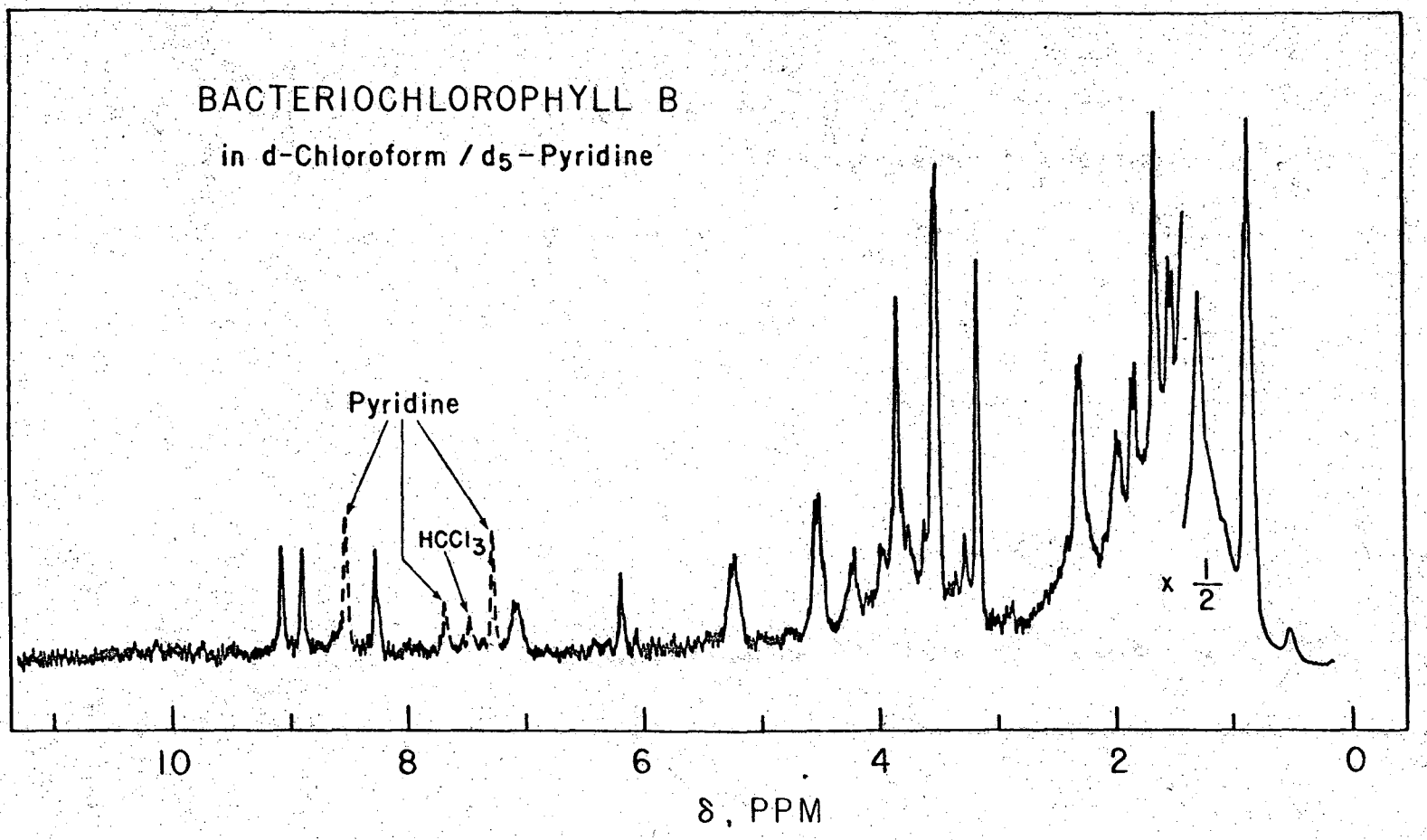
XBL714-5107

Sauer & Baumgarten
Fig. 2

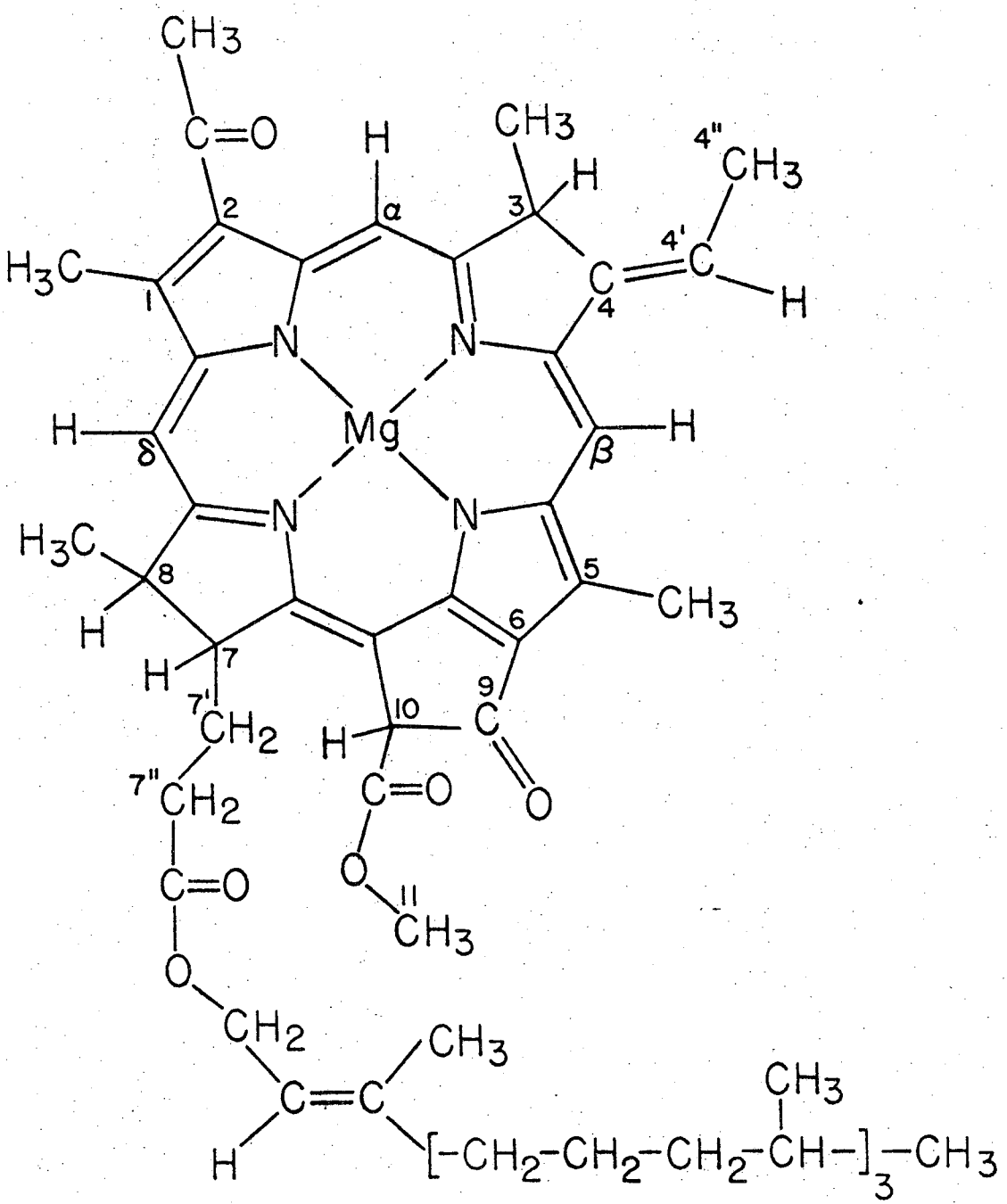


XBL 714-5105

Sauer & Baumgarten
Fig. 3



Sauer & Baumgarten
Fig. 4



BACTERIOCHLOROPHYLL B

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Fig. 5

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