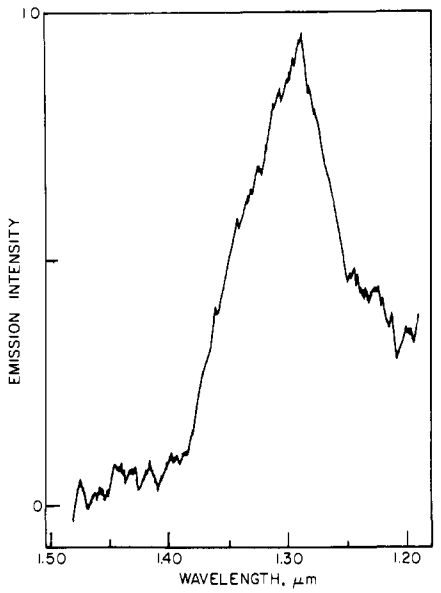

Figure 3. Emission spectrum of (0,0) $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ of molecular oxygen originating from the reaction of finely divided suspension of KO_2 in CCl_4 with water. The apparent peak position at 1.284 μm is a shift from the true position of 1.268 μm due to the combined monochromator–detector spectral sensitivity.

Reagent, Mallinckrodt, Paris, KY), were suspended by constant stirring. The reaction cell was designed such that the suspension of KO_2 in CCl_4 flows on one side of a fritted disk, the side facing the monochromator. Water flows continuously on the other side of the disk. The whole assembly is placed inside a closed wooden box lined with black paper, and the experiment takes place in a darkened room.

Figure 1 is the chemiluminescence spectrum of the H_2O_2/OCl^- reaction. The emission peak at 1.29 μm is the (0,0) $^1\Delta_g \rightarrow {}^3\Sigma_g$ transition, shifted from the true position of 1.268 μm due to the combined monochromator–detector spectral sensitivity. Figure 1 depicts the wavelength calibrator for the present experimental setup.

Figure 2 is a recording of time vs. intensity of emission at 1.29 μm. The emission appears when the suspended KO_2 particles in CCl_4 begins to flow over the wet fritted disk. The electronics were set at the shortest possible time constant with poor but acceptable signal-to-noise ratio so that the rise and fall of the emission with the start and stop of the CCl_4 suspension of KO_2 over the wet disk is clearly displayed.

Figure 3 is a spectrum of the emission scanned from 1.40 to 1.20 μm showing a peak at 1.284 μm, corresponding to the O_2 (0,0) transition $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ in this experimental setup. The heterogeneity of the reaction presents difficulties in maintinaing steady-state reaction conditions. A higher integration time constant for the electronics was used to improve the signal-to-noise ratio in obtaining this spectrum than in the time–intensity curve.

In a previous theoretical appraisal of the disproportionation reaction of the superoxide anion, several factors became evident:[2c] (i) The reaction is thermodynamically favored both by free energy and by entropy considerations. (ii) The nature of the product, i.e., whether the molecular oxygen is electronically excited or in the ground state depends largely on the dielectric of the solvent medium. (iii) However, as the yield of excited product increases with increasing solvent dielectric constant, the generation of the short-lived and easily quenched $^1\Sigma_g^+$ singlet oxygen becomes predominant. (iv) Moreover, superoxide anion quenching of $^1O_2$ by electron-transfer reaction is four orders of magnitude more efficient than solvent quenching for O_2 ($^1\Delta_g$). (v) Furthermore, unlike solvent quenching of O_2 ($^1\Sigma_g^+$) which is theoretically predicted to proceed to O_2 ($^1\Delta_g$) excited state,[7] electron-transfer quenching by O_2^- is directly to the ground state. We plan to extend these investigations to other electron-transfer reactions of the superoxide anion, particularly those involving metal ions, and to evaluate the efficiency of singlet oxygen generation in these electron-transfer reactions.

A large number of reports have appeared postulating the involvement of singlet oxygen and/or superoxide anion in biological processes, such as the biosynthesis of prostaglandins,[8] microsomal lipid oxidase reactions,[9,10] xanthine oxidase[11-13] and phagocytosing polymorphonuclear leukocytes,[14] and the fertilization of sea urchin eggs.[15] These reports are currently based on indirect evidence of chemical or luminescence studies. We believe that with the new spectrometer and improved data-processing accessories it will be possible to provide unequivocal evidence of singlet oxygen in such systems by monitoring directly the singlet oxygen ($^1\Delta_g$) emission.

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Structures of Eleven Zervamicin and Two Emerimicin Peptide Antibiotics Studied by Fast Atom Bombardment Mass Spectrometry[1,2]

Kenneth L. Rinehart, Jr.,* Larry A. Gaudioso, Michael L. Moore, Ramesh C. Pandey, and J. Carter Cook, Jr.

School of Chemical Sciences
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801

Michael Barber, R. Donald Sedgwick, Robert S. Bordoli, and Andrew N. Tyler

University of Manchester
Institute of Science and Technology
Manchester, United Kingdom M60 1QD

Brian N. Green

VG Analytical Ltd.
Altrincham, United Kingdom WA14 5RZ

Received June 15, 1981

We have recently revised the previously assigned[3] structures of alamethicins I and II to **1** and **2**[4] and have assigned the structures of the peptaibophol antibiotics emerimicins III and IV[5] and antiamoebins I[6] and II[7] as **3–6**, respectively. These structures

(1) Presented in part at the 29th Annual Conference on Mass Spectrometry and Allied Topics, Minneapolis, MN, May 24–29, 1981.
(2) Paper 7 in the series Peptaibophol Antibiotics. Paper 6 ref 9.
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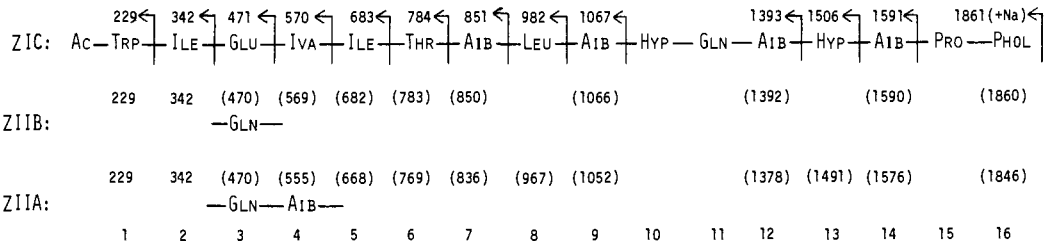
Scheme I. FABMS Fragment Ions Observed for Zervamicins IC, IIB, and IIA (ZIC, ZIIB, ZIIA)[a,b]



[a] See also Table II. [b] The sequences of ZIIB and ZIIA are the same as that of ZIC except for the amino acid replacements shown. Parentheses around specific ZIIB and ZIIA ions indicate those masses are shifted from the ions for ZIC.

were assigned by using methods based largely on mass spectrometric techniques, including high-resolution field desorption and electron impact mass spectrometry (HRFDMS, HREIMS) and gas chromatography/mass spectrometry (GC/HRMS).[8,9]

In an attempt to determine the structural features responsible for the remarkable pore-forming activity[10] of this class of antibiotics, we have been examining other peptaibophols. In particular, the zervamicin[11] and emerimicin II[12] complexes, from *Emericellopsis salmosynnemata* and *E. microspora*, respectively, are of considerable interest since they have reduced pore-forming activity[13] but enhanced antibacterial activity,[11,12] and contain both tryptophan and threonine,[11,12,14] which are not found in other known peptaibophols. Unfortunately, the presence of tryptophan renders these antibiotics much less amenable to both mass spectrometry and acidolytic cleavage into fragments. Very poor results are obtained from both FDMS and EIMS of the intact peptides.

Very recently, a new mass spectrometric technique called fast atom bombardment (FAB)[15,16] has been developed for dealing with nonvolatile, thermally labile molecules. FABMS involves bombarding the sample in the ion source with highly energetic argon atoms (2–10 KeV) and has been applied to bradykinin and other peptides.[17] We have now employed FABMS successfully in the present study of previously intractable peptaibophols and wish to report here the structures of zervamicins IA, IB, IB′, IC, IIA, IIB, II-1, II-2, II-3, II-4, and II-5 (**7–17**, respectively) and emerimicins IIA and IIB, which are shown to be identical with zervamicins IIA and IIB.

Crude zervamicin I, an acidic peptide,[11] was purified by reversed-phase high-performance liquid chromatography on Ultrasphere-ODS (Altex) (HPLC) by using methanol–water–2-propanol–acetic acid (50:34:16:0.1) to yield zervamicin IC, the major component, and zervamicins IA, IB, and IB′, the minor components. Emerimicin II[12] and zervamicin II[11] were similarly separated into two major components each (IIA and IIB), and five additional neutral zervamicins (II-1, II-2, II-3, II-4, and II-5) were also isolated by using methanol–water–2-propanol (52:32:16). Furthermore, the major components of emerimicin II and zervamicin II coelute and give identical amino acid compositions (Table I)[18] and FAB mass spectra (Table II).[19] Therefore, we conclude that emerimicins IIA and IIB are identical with zervamicins IIA and IIB, and the zervamicin nomenclature will be used to identify these two peptide mixtures.

Table I. Amino Acid Compositions of the Zervamicins[a]

amino acid[b]	zervamicin										
	IA	IB	IB′	IC	IIA	IIB	II-1	II-2	II-3	II-4	II-5
Aib	4	4	4–5	4	4–5	4	4–5	4–5	4–5	4	4
Iva	1	1		1		1				1	1
Val	1	1					1	1	1	1	1
Ile	1	1	2	2	2	2	1	2	1	1	2
Leu	1	1	1	1	1	1	1		1	1	
Pro	1	1	1	1	1	1	1	1	1	1	1
Thr	1	1	1	1	1	1	1	1	1	1	1
Hyp	2	2	2	2	2	2	2	2	2	2	2
Phol[c]	1	1	1	1	1	1	1	1	1	1	1
Glx	2	2	2	2	2	2	2	2	2	2	2
Trp	1	1	1	1	1	1	*d*	*d*	*d*	*d*	*d*

[a] Estimated from GC traces of *N*-trifluoroacetyl *n*-butyl ester derivatives obtained from total acid hydrolyzates. [b] In order of elution from Tabsorb. [c] Amino alcohol. [d] Trp is sometimes degraded during the hydrolysis.

As in our past studies,[4-7,9] amino acids were identified by FDMS of the total acid hydrolyzate (from ca. 1 mg of antibiotic) and GC/MS of their trifluoroacetyl (TFA) *n*-butyl ester derivatives (Tabsorb, Regis Chemical Co.) and were quantitated by GC. Absolute configurations were assigned by GC of their TFA methyl esters on a packed chiral column of 10% *N*-lauroyl-*N*′-*tert*-butyl-L-valinamide (for Val, Ile, Leu, Thr, Hyp, and Glu) or of their TFA butyl esters (Pro, Iva), TFA methyl esters (Trp), or pentafluoropropionyl (PFP) butyl esters (Phol) on a chiral capillary column (RSL-007, Alltech Associates). Zervamicins IIA, IIB, and IC all yield 2 mol each of L-Ile, L-Hyp, and L-Glu and 1 mol each of L-Leu, L-Pro, L-Thr, L-Trp, and L-Phol (Table I). Zervamicins IIB and IC additionally yield 4 mol of Aib and 1 mol of D-Iva, while zervamicin IIA yields 5 mol of Aib and no Iva.

Molecular weights of zervamicins IC, IIA, and IIB were assigned as 1838, 1823, and 1837 on the basis of their respective M + Na ions at *m/z* 1861, 1846, and 1860 in the positive ion FAB mass spectra and their M − H ions at 1837, 1822, and 1836 in the negative ion FAB mass spectra (Figures 1 and 2). Intense fragment ions in the positive ion FAB mass spectra[17] at *m/z* 58, 70, 72, 86, and 130 were indicative of the presence of Aib, Pro, Iva (or Val), Ile (or Leu or Hyp), and Trp in the peptide and could have served to identify those amino acids if their presence had not previously been established. In addition, the positive ion FAB mass spectrum of zervamicin IC (Figure 1) also gave quite clearly the acyl cleavage ions shown in Scheme I, defining the entire sequence of amino acids except for distinction among the isobaric ions due to Leu, Ile, and Hyp and the sequence in the tripeptide unit involving amino acids 10, 11, and 12.

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(18) The abbreviations Aib, Iva, and Hyp refer to α-aminoisobutyric acid, isovaline (α-ethylalanine), and 4-hydroxyproline, respectively.
(19) Obtained on a Micromass ZAB 2F mass spectrometer employing 6-KeV argon atoms (from argon ions charge exchanged with argon gas) directed onto a matrix prepared from a small amount (ca. 1 μg) of sample dispersed in glycerol on a tungsten ribbon. Spectra were recorded oscillographically.

Table II. Ions Observed in Positive Ion FAB Mass Spectra of the Zervamicins

	acyl cleavage ions, *m/z*													"molecular" ions, *m/z*			
Z[a]	Ac–1	2	3	4	5	6	7[b]	8	9	10,11	12	13	14	15,16	M + Na	M + K	M – H[d]	M[d]
IA	229	342	471	570	669		837		1053								1823	1824
IB	229	328	457	556	669		837		1053								1823	1824
IB′	229	342	471	556			837		1053								1823	1824
IC	229	342	471	570	683	784	851	982	1067		1393	1506	1591		1861	1877	1837	1838
IIA	229	342	470	555	668	769	836	967	1052		1378	1491	1576		1846	1862	1822	1823
IIB	229	342	470	569	682	783	850		1066		1392		1590		1860	1876	1836	1837
II-1	229	342	470	555	654	755	822[c]	953	1038								1808	1809
II-2	229	342	470	555	668	769	836	953	1038								1808	1809
II-3	229	328	456	541	654	755	822	953	1038		1364		1562				1808	1809
II-4	229	342	470	569	668	769	836	967	1052								1822	1823
II-5	229	342	470	569	682	783	850[c]	967	1052								1822	1823

[a] Zervamicin. [b] Acyl cleavage – H_2O. [c] Acyl cleavage also observed at *m/z* 840 (II-1) and 858 (II-5). [d] Negative ions.

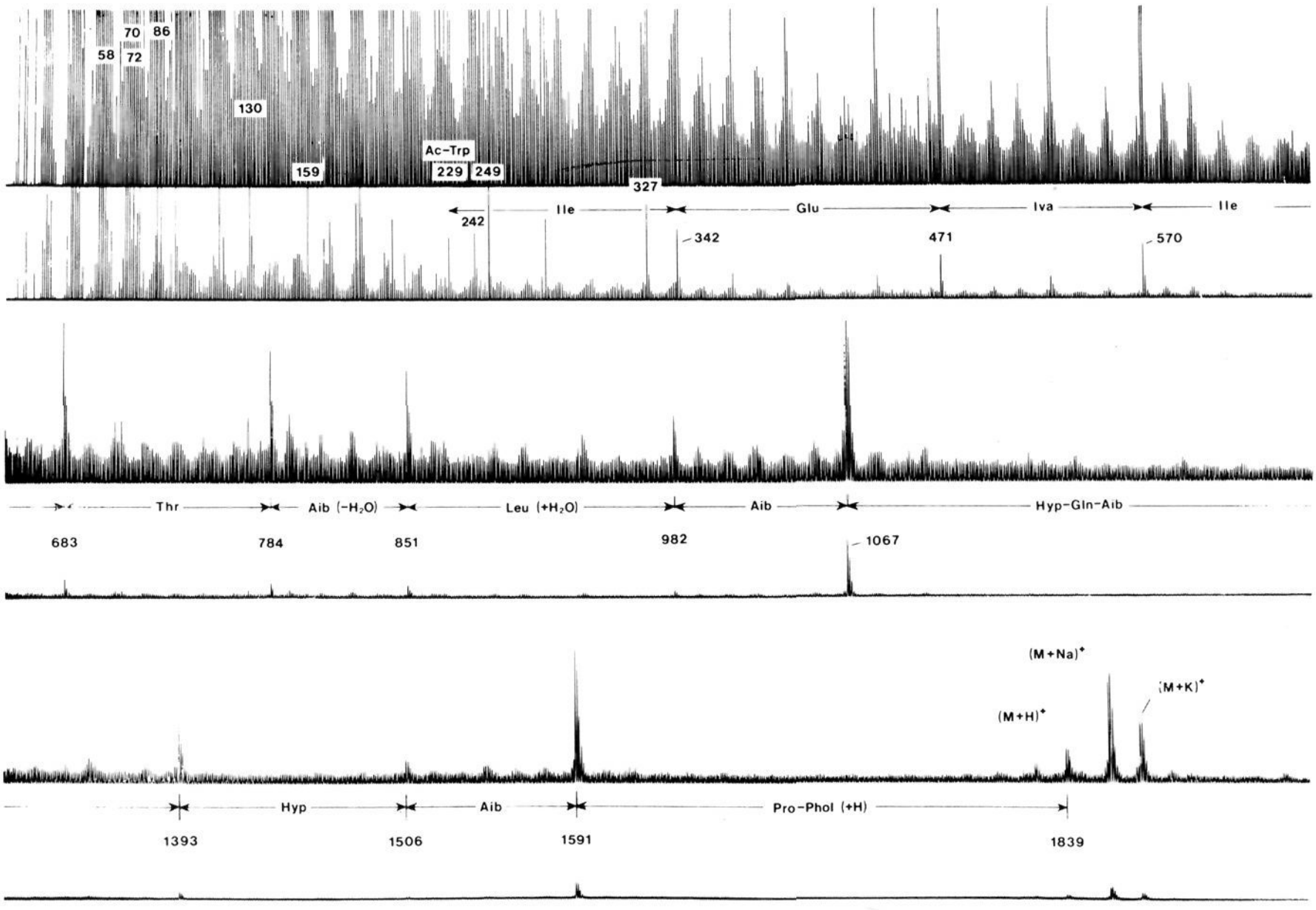

Figure 1. Positive ion FAB mass spectrum of zervamicin IC. Ions at *m/z* 93, 185, 277, etc., are due to $(G_n + H)^+$, where G = glycerol.

The Leu (Ile) vs. Hyp positions were partially distinguished by an accurate mass measurement[20] carried out on the *m/z* 1067 ion of zervamicin IC, which gave the value 1067.6088 (calcd 1067.6023 for $C_{53}H_{83}N_{10}O_{13}$), indicating both Hyp residues were absent from this ion; thus, one Hyp is at position 13 and the other at 10, 11, or 12. Preferential mass spectral cleavages[5,6] between amino acids 9 and 10, 12 and 13, and 14 and 15 would be in keeping with Hyp at positions 10 and 13, Pro at 15, and indeed, the only other prominent peaks above *m/z* 230 were at *m/z* 242, 249, and 327 due to Hyp-Gln + H, Pro-Phol + H_2, and Hyp-Gln-Aib + H, respectively. This location for Hyp-10 was confirmed by a hydrolytic experiment described below. These assignments complete the structure of zervamicin IC, except for the disposition of Leu and Ile at positions 2, 5, and 8, which will be established below.

(20) High-resolution measurement was difficult but was successfully accomplished by peak matching the very intense sample peak (*m/z* 1067) vs. the M + H ion of gramicidin S (1141.71376).

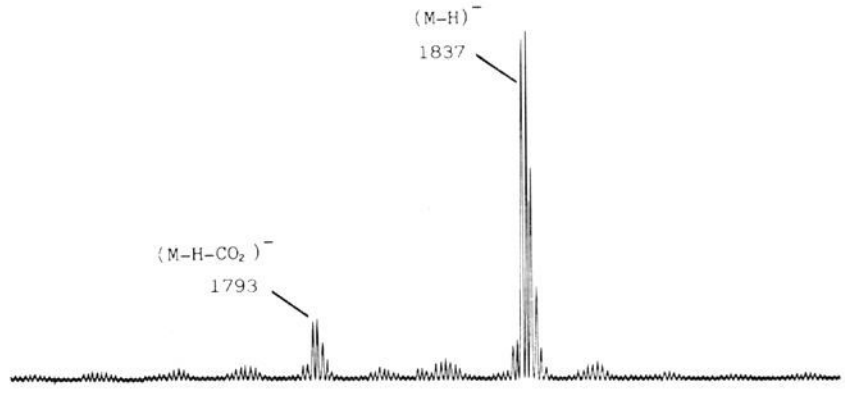

Figure 2. Molecular ion region of the negative ion FAB mass spectrum of zervamicin IC.

The assignment of a structure for the neutral peptide zervamicin IIB follows, since the FAB mass spectrum shows a shift of ions above *m/z* 342 to positions 1 amu lower, indicating the replacement of Glu at position 3 in zervamicin IC with a Gln residue (Scheme I). Similarly, the sequence of the other major neutral

Chart I

	1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
1:	Ac-Aib-Pro-Aib-Ala-Aib-Ala-Gln-Aib-Val-Aib-Gly-Leu-Aib-Pro-Val-Aib-Aib-Glu-$^{\alpha}$Gln-Phol
2:	Ac-Aib-Pro-Aib-Ala-Aib-Aib-Gln-Aib-Val-Aib-Gly-Leu-Aib-Pro-Val-Aib-Aib-Glu-$^{\alpha}$Gln-Phol
3:	Ac-Phe-Aib-Aib-Aib-Val-Gly-Leu-Aib-Aib-Hyp-Gln-Iva-Hyp-Ala-Phol
4:	Ac-Phe-Aib-Aib-Aib-Val-Gly-Leu-Aib-Aib-Hyp-Gln-Iva-Hyp-Aib-Phol
5:	Ac-Phe-Aib-Aib-Aib-Iva-Gly-Leu-Aib-Aib-Hyp-Gln-Iva-Hyp-Aib-Pro-Phol
6:	Ac-Phe-Aib-Aib-Aib-Iva-Gly-Leu-Aib-Aib-Hyp-Gln-Iva-Pro-Aib-Pro-Phol
7(ZIA):	Ac-Trp-Ile-Glu-Iva-Val-Thr-Aib-Leu-Aib-Hyp-Gln-Aib-Hyp-Aib-Pro-Phol
8(ZIB):	Ac-Trp-Val-Glu-Iva-Ile-Thr-Aib-Leu-Aib-Hyp-Gln-Aib-Hyp-Aib-Pro-Phol
9(ZIB'):	Ac-Trp-Ile-Glu-Aib-Ile-Thr-Aib-Leu-Aib-Hyp-Gln-Aib-Hyp-Aib-Pro-Phol
10(ZIC):	Ac-Trp-Ile-Glu-Iva-Ile-Thr-Aib-Leu-Aib-Hyp-Gln-Aib-Hyp-Aib-Pro-Phol
11(ZIIA):	Ac-Trp-Ile-Gln-Aib-Ile-Thr-Aib-Leu-Aib-Hyp-Gln-Aib-Hyp-Aib-Pro-Phol
12(ZIIB):	Ac-Trp-Ile-Gln-Iva-Ile-Thr-Aib-Leu-Aib-Hyp-Gln-Aib-Hyp-Aib-Pro-Phol
13(ZII-1):	Ac-Trp-Ile-Gln-Aib-Val-Thr-Aib-Leu-Aib-Hyp-Gln-Aib-Hyp-Aib-Pro-Phol
14(ZII-2):	Ac-Trp-Ile-Gln-Aib-Ile-Thr-Aib-Val-Aib-Hyp-Gln-Aib-Hyp-Aib-Pro-Phol
15(ZII-3):	Ac-Trp-Val-Gln-Aib-Ile-Thr-Aib-Leu-Aib-Hyp-Gln-Aib-Hyp-Aib-Pro-Phol
16(ZII-4):	Ac-Trp-Ile-Gln-Iva-Val-Thr-Aib-Leu-Aib-Hyp-Gln-Aib-Hyp-Aib-Pro-Phol
17(ZII-5):	Ac-Trp-Ile-Gln-Iva-Ile-Thr-Aib-Val-Aib-Hyp-Gln-Aib-Hyp-Aib-Pro-Phol

component, zervamicin IIA, can be deduced from the FAB mass spectrum, which indicates that the Iva at position 4 of zervamicin IIB is replaced by Aib (Scheme I).

Partial hydrolysis of zervamicin IIB in trifluoroacetic acid, a procedure we earlier showed to cleave selectively Aib–Hyp and Aib–Pro bonds,[4-7,9] yielded several oligopeptides which were separated by HPLC (methanol–water–acetic acid, 70:29:1) and identified by GC/MS of the derivatized total acid hydrolyzate. The oligopeptides included the nonapeptide Ac-Trp-Ile(Leu)-Gln-Iva-Ile(Leu)-Thr-Aib-Leu(Ile)-Aib (containing no Hyp), the dodecapeptide Ac-Trp-Ile(Leu)-Gln-Iva-Ile(Leu)-Thr-Aib-Leu-(Ile)-Aib-Hyp-Gln-Aib (containing 1 Hyp), and the tetradecapeptide Ac-Trp-Ile(Leu)-Gln-Iva-Ile(Leu)-Thr-Aib-Leu(Ile)-Aib-Hyp-Gln-Aib-Hyp-Aib (containing 2 Hyp's). The dipeptide fragments Hyp-Aib and Pro-Phol and the tripeptide Hyp-Gln-Aib were also detected as major components of the partial hydrolyzate by GC/MS following derivatization.[4] These results confirm the location of Hyp at positions 10 and 13, Pro at 15, Gln at 11, and Aib at 9, 12, and 14. Partial hydrolysis of zervamicin IIB in 8.0 N hydrochloric acid–methanol also proved useful, since the tetrapeptide Thr-Aib-Leu(Ile)-Aib was identified by GC/MS of the derivatized hydrolyzate, confirming the proposed sequence at positions 6–9.

The remaining problem, concerning the location of the Ile and Leu residues in these peptides, was solved by studying several minor components of the zervamicin complexes. Hydrolysis, derivatization, and GC/MS indicated the amino acid compositions shown in Table I, and FABMS gave molecular ions and characteristic ions for several amino acids as well as fragment ions indicating isomorphous replacement, as shown in Table II. Particularly significant are the amino acid compositions of zervamicins IB and II-3 in which Val replaces one Ile residue of zervamicins IC, IIA, and IIB (Table I) and which can be shown from FAB fragment ions (Table II) to be the amino acid at position 2, i.e., Ile should be at position 2 in zervamicins IC, IIA, and IIB. Similarly, in zervamicins IA, II-1, and II-4 Val replaces an Ile of zervamicins IC, IIA, and IIB (Table I) which should be at position 5 (Table II), while in zervamicins II-2 and II-5 Val replaces a Leu residue of zervamicins IC, IIA, and IIB (Table I) which should be at position 8 (Table II).

As noted at the outset, zervamicin II shows considerably reduced membrane pore-forming ability and considerably enhanced antibacterial activity compared to alamethicins, antiamoebins, and emerimicins III and IV. Comparing the sequences of the zervamicins with those of **1–6** (and most particularly of **5** and **6**), there are obvious regions of close similarity of zervamicins with the antiamoebins (amino acids 7–16), as well as regions of difference (amino acids 1–6). Interchange of the nonpolar amino acids Aib, Iva, Leu, and Ile is not regarded as of primary importance nor is chain shortening, as in emerimicins III and IV (**3** and **4**). Which of the major replacements (Trp-Phe, Thr-Gly, Gln-Aib) is (are) responsible for these major alterations of bioactivity will be the subject of future reports. It should be noted, however, that all of the replacements are in the direction of forming a more polar N terminus in the zervamicin antibiotics (vs. **3–6**). The present communication shows that relatively minor variations in amino acid composition and sequence have profound effects and that these and related antibiotics can probably be studied optimally by FABMS combined with the previously employed[4-9] GC/MS techniques.

Acknowledgment. This work was supported in part by grants from the National Institute of Allergy and Infectious Diseases (AI 04769), the National Cancer Institute (CA 11,388), and the National Institute of General Medical Sciences (GM 27029). We thank Dr. A. D. Argoudelis, The Upjohn Co., for samples of zervamicins I and II and emerimicin II.

Hydrogenation on the Hindered Face of *syn*-Sesquinorbornene Photosensitized by Acetone

Paul D. Bartlett,* Antonius A. M. Roof, and William J. Winter

Department of Chemistry, Texas Christian University Fort Worth, Texas 76129

Received February 17, 1981
Revised Manuscript Received August 17, 1981

In addition to unusual steric effects in the reactions of syn[1] and anti[2] isomers of sesquinorbornene, it has recently been found by X-ray crystallography[3a] that two derivatives of *syn*-sesquinorbornene (**1**) show a hingelike bending of the double bond with a dihedral angle of 162–164° between the plane of carbon atoms 4a, 8a, 1, 4 and that of atoms 4a, 8a, 5, 8. Careful examination of the intermolecular interactions suggested no way in which the deformation could be due to forces between molecules within the crystal.[3]

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