REVISED STRUCTURE OF A53868A

ANN H. HUNT and THOMAS K. ELZEY

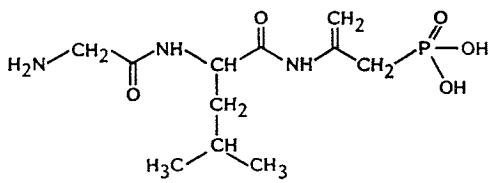
Lilly Research Laboratories,
Eli Lilly and Company,
Indianapolis, Indiana 46285, U.S.A.

(Received for publication February 3, 1988)

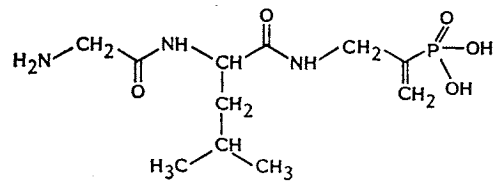
A53868A is a novel phosphorus-containing antibiotic obtained by fermentation of *Streptomyces luridus* NRRL 15101; the product has a broad-spectrum antimicrobial activity[1]. The molecular formula of $C_{11}H_{22}N_3O_5P$ (MW 307) contains units of glycine, leucine, and $C_3H_7NO_3P$; mass spectral fragmentation observations and ^1H NMR studies were combined to suggest the structure **1**[1].

However, attempts to synthesize a series of analogs of GLAPP (**1**) prompted a re-examination of the structure elucidation of the parent compound, A53868A. The pattern of carbon-phosphorus coupling constants in the ^{13}C NMR spectrum (see Table 1) requires that the structure of A53868A be revised to **2**.

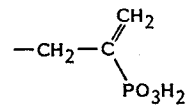
The carbon-phosphorus coupling of 190.1 Hz indicates that phosphorus is directly bonded to the non-protonated carbon, while the two methylene carbons show only long-range coupling to the phosphorus[2]. Therefore, the propenyl-phosphonate fragment must have the structure **3** rather than **4**.



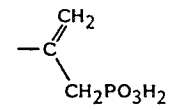
Glycyl-leucyl-2-amino-2-propenyl-phosphonate (GLAPP, **1**)



A53868A (**2**)



3



4

Acknowledgments

We thank Mr. D. C. THOMPSON for calling this problem to our attention and Dr. R. D. JOHNSON for providing the sample of A53868A.

References

1) JOHNSON, R. D.; R. S. GORDEE, R. E. KASTNER, S. H. LARSEN & E. E. OSE: Leucylaminopropenyl phosphonate immunomodulating agents. Brit. UK Pat. Appl. 2,127,413, 1984 [Chem. Abstr. 101: 88837r, 1984]
2) BREITMAIER, E. & W. VOELTER: Carbon-13 NMR Spectroscopy (2nd Ed.). pp. 106~110, Verlag Chemie, New York, 1978

Table 1. ^{13}C NMR data for A53868A in D_2O solution (67.9 MHz, internal reference; dioxane, 67.4 ppm).

Assignment	^{13}C δ (ppm)	Multiplicity	Correlated H's*	J (^{13}C-^{31}P) (Hz)
Gly C=O	167.9	s	—	
Gly α	41.2	t	3.90	
Leu C=O	174.2	s	—	8.7
Leu α	54.2	d	4.45	
Leu β	40.6	t	1.69	
Leu γ	25.2	d	1.69	
Leu δ	22.9	q	0.95,	
Leu δ	21.7	q	0.93	
C	135.7	s	—	190.1
CH_2	117.1	t	6.20, 5.70	10.5
CH_2	52.9	t	3.52	5.3

* Assigned by single-frequency irradiation experiments.