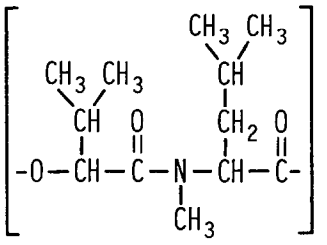
Tetrahedron Letters No. 46, pp 4049 - 4050, 1977. Pergamon Press. Printed in Great Britain.

SYNTHESIS OF BASSIANOLIDE

Masaharu KANAOKA, Akira ISOGAI and Akinori SUZUKI*
Department of Agricultural Chemistry, The University of Tokyo,
Tokyo 113, Japan

(Received in Japan 3 September 1977; received in UK for publication 26 September 1977)

Recently we have reported the isolation and structure elucidation of a new insecticidal cyclodepsipeptide bassianolide(1a)[1], which was produced by entomopathogenic fungi *Beauveria bassiana* and *Verticillium lecanii*.

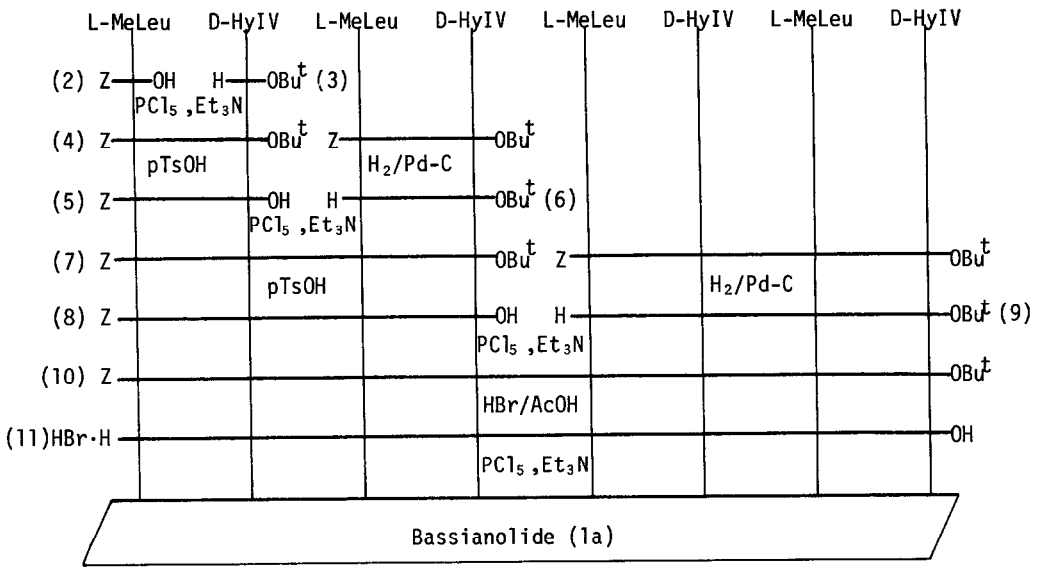


1a n=4
1b n=5

Despite 1a has a primarily symmetrical structure, five N-methyl signals in the PMR spectrum and totally sixty signals in the CMR spectrum were observed in a $CDCl_3$ solution. So structure 1b was not entirely neglected for bassianolide by considering these spectra. Then a detailed NMR study[2] and a total synthesis of 1a were attempted to confirm the determined structure of bassianolide. The present report describes the synthesis of bassianolide.

Bassianolide was prepared according to Scheme 1 starting with carbobenzoxy-L-N-methylleucine(2) and t-butyl-D-α-hydroxyisovalerate(3) by the analogous methods used previously for preparation of enniatin B[3]. The free octadepsipeptide(11) was cyclized by the acid chloride method in benzene under a highly diluted condition and the product was purified on a silica gel column chromatography eluted with benzene-ethyl acetate system to give pure 1a as an amorphous solid($[\alpha]_D^{22}$-69°(c=3.3,$CHCl_3$)).

Scheme 1



Yield(%) (4) 89 (5) 97 (6) 63 (7) 78 (8) 49 (9) 67 (10) 68 (1a) 62

The specific optical rotation, IR-, PMR- and mass spectra, and also the biological activities of the synthetic bassianolide were in agreement with those of the natural product. Thus, the structure of bassianolide was unequivocally established as 1a.

Acknowledgement

The authors wish to express their thanks to Emeritus Professor S. Tamura of The University of Tokyo for his valuable suggestions and encouragement.

References

1) A. Suzuki, M. Kanaoka, A. Isogai, S. Murakoshi, M. Ichinoe and S. Tamura, Tetrahedron Letters, 2167(1977).

2) in preparation.

3) Pl. A. Plattner, K. Vogler, R. O. Studer, P. Quitt and W. Keller-Shierlein, Helv. Chim. Acta, 46, 927(1963)