

THE STRUCTURE OF THE CYCLODEPSIPEPTIDE, ANGLIDE

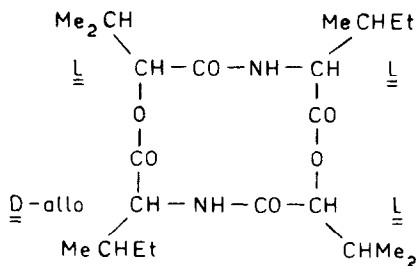
C.G. Macdonald and J.S. Shannon
 Division of Coal Research, C.S.I.R.O., P.O. Box 175, Chatswood, N.S.W., Australia

(Received 31 August 1964)

RECENTLY a new depsipeptide, anglide, was isolated from a species of Pithomyces. It gave on acid hydrolysis a mixture of L-isoleucine, D-allo-isoleucine, and L- α -hydroxy- β -methylbutyric acid¹. Continuing our studies on the mass spectrometry of depsipeptides^{2,3} we have obtained results which permit assignment of a structure for anglide.

Fig. 1 presents the mass spectrum of anglide, the figures in brackets after the m/e values being the shifts which the peaks display in the spectrum of anglide -N,N-d₂ prepared by exchange of anglide with D₂O. Since the micro-analyses¹ indicated an empirical formula (C₁₁H₁₉NO₃)_n the small peak at m/e 426 was considered to be the molecular ion peak making n equal to 2 and anglide a cyclotetradepsipeptide.

Russian workers have recently shown⁴ that compounds of this class give weak molecular ion peaks. If anglide has structure I, which is consistent with the chemical evidence, it is possible to account for its mass spectrum in



I

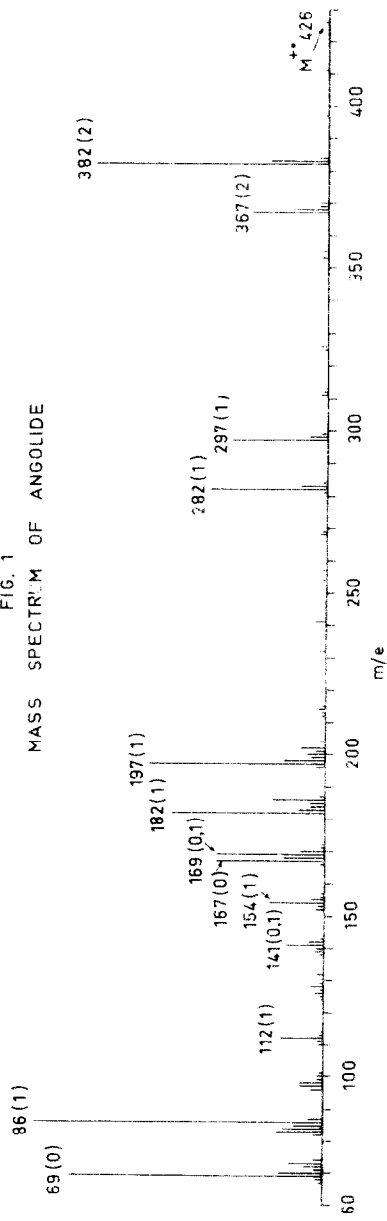
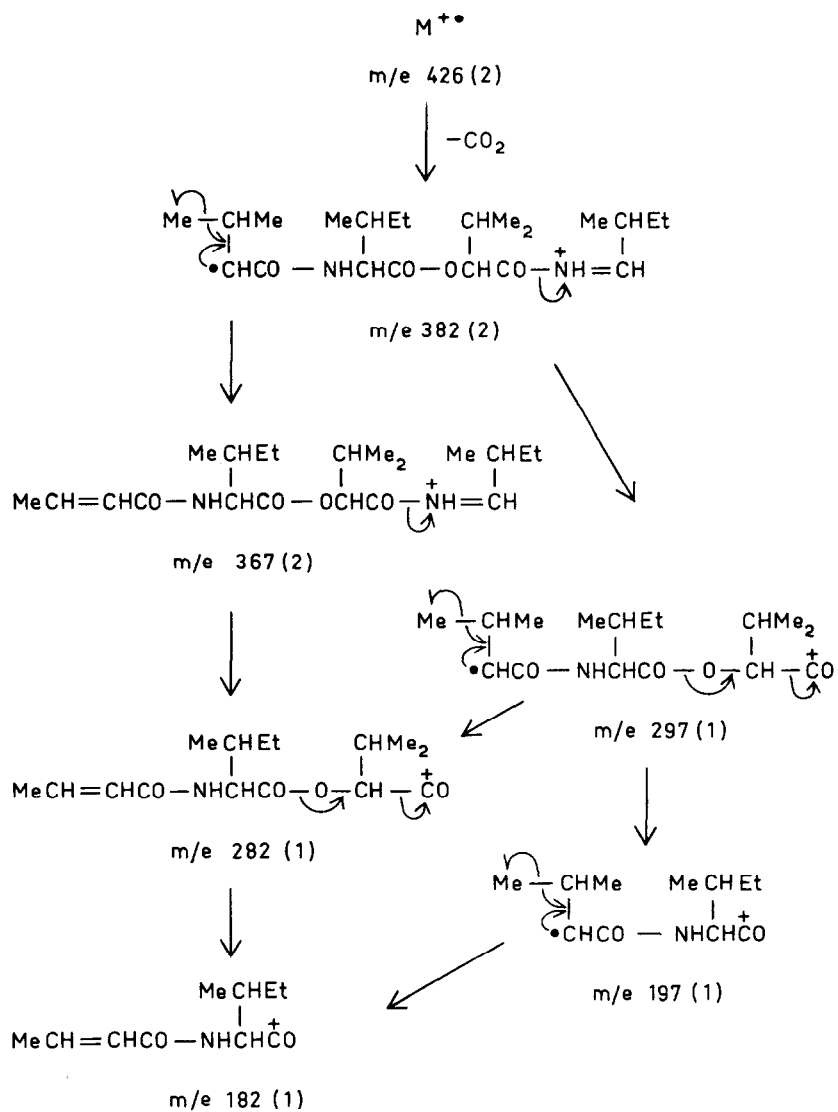
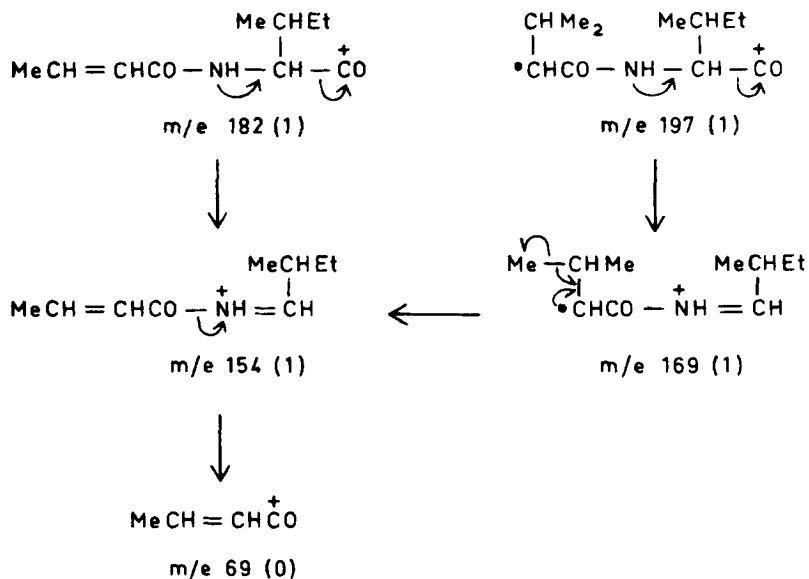
FIG. 1
MASS SPECTRUM OF ANGOUIDE

FIG. 2

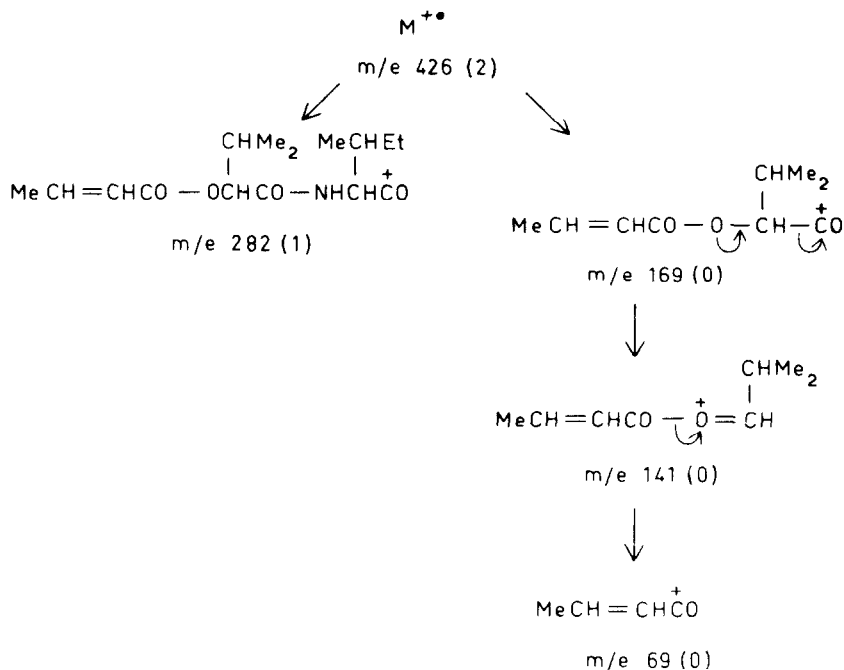


terms of ion reactions recently proposed to rationalize the mass spectra of series of cyclodepsipeptides of known structure. Thus the peaks at m/e 382(2), 367(2), 297(1), 282(1), 197(1), and 182(1) are to be expected (see Fig. 2) as a result of the " CO_2 type of fragmentation"⁴ of Structure I.

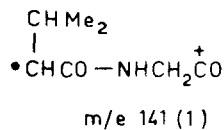
The ions of m/e 197(1) and 182(1) could give rise to those of m/e 169(1), 154(1), and 69(0) as follows:



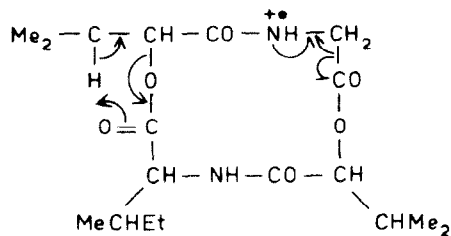
Reactions analogous to the reactions l, n, and p proposed² for sporides-molides I and II could produce ions of m/e 282(1), 169(0), and 141(0) respectively, and the latter is another possible precursor of the ion of m/e 69(0).



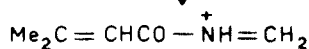
Loss from the molecular ion, the ion of $m/e \ 382(2)$ (there is a metastable peak at $326^2/382$), the ion of $m/e \ 297(1)$, or the ion of $m/e \ 197(1)$, of a C_4 side chain by reaction b^2 followed by ketonization could lead by reactions similar to those depicted in Fig. 2 to an ion of $m/e \ 141(1)$ with the structure:



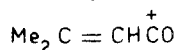
Loss of a C_4 side chain from the molecular ion by reaction b^2 followed by ketonization would give an ion of $m/e \ 370(2)$, which could undergo the following reactions to produce ions of $m/e \ 112(1)$ and $83(0)$:



m/e 370 (2)

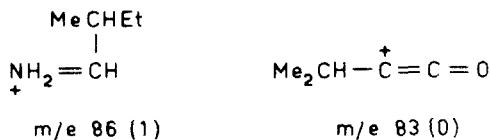


m/e 112 (1)



m/e 83 (0)

Operation of the "morpholine type" of cyclodepsipeptide fragmentation⁴ on Structure I could give rise to ions of m/e 86(1) and 83(0) with the following structures:



The alternative structure for angolide with an ester-ester-amide-amide sequence of linkages is eliminated by the fact that rupture of only the ester bonds of angolide with hydrazine gives rise to two hydrazides, one containing isoleucine and the other allo-isoleucine (Russell, personal communication).

REFERENCES

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4. N.S. Wulfson, V.A. Fuchkov, V.N. Bochkarev, B.V. Rozinov, A.M. Zyakoon, M.M. Shemyakin, Yu. A. Orchinnikov, V.T. Ivanov, A.A. Kiryushkin, E.I. Vinogradova, M.Yu. Feigina, and N.A. Aldanova, Tetrahedron Letters No.17, 951 (1964).