

MASS SPECTRA OF CYCLIC DEPSIPEPTIDES: SPORIDESMOLIDES

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THIS paper presents results of the mass-spectral investigation of some cyclic depsipeptide<sup>†</sup> metabolic products of the fungus Pithomyces chartarum. Good mass spectra of sporidesmolide I (A)<sup>2</sup> and sporidesmolide II (B)<sup>3,4</sup> have been obtained and rationalized in terms of chemical structure. The proposed mechanisms for the ionic fragmentation reactions may have wider application in structural studies with other depsipeptides.

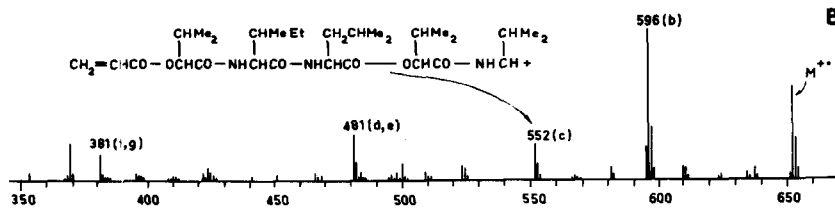
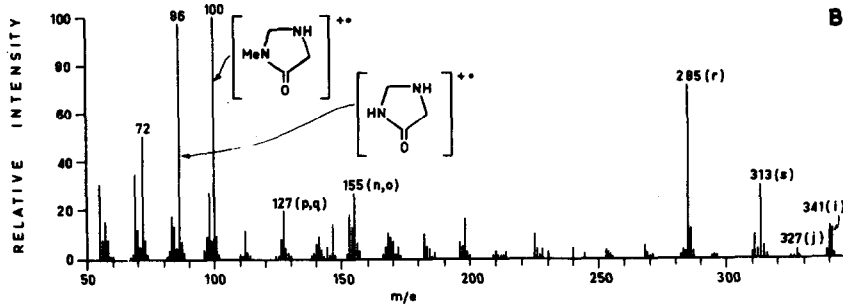
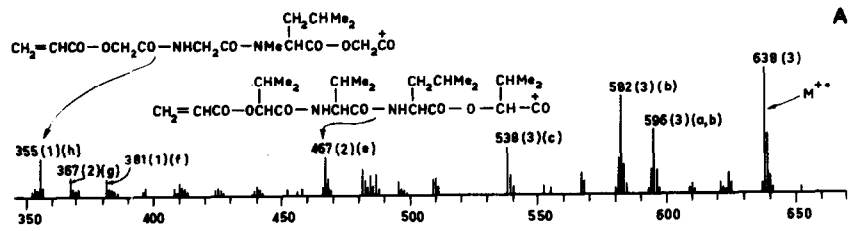
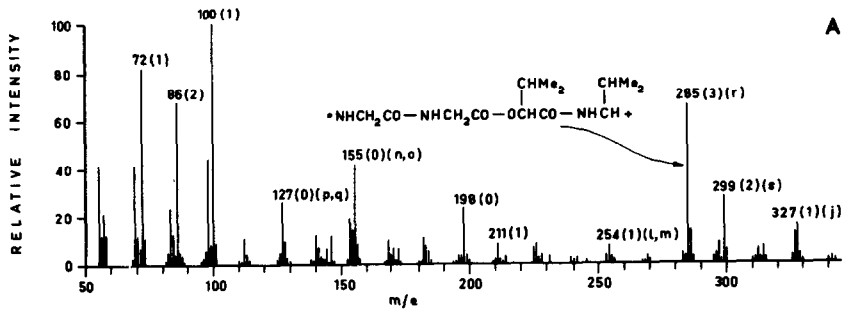
The mass spectra were obtained by introduction of small samples (<0.5 mg) directly into the ion source, where they were evaporated on the fringe of the ionizing-electron beam. The spectra had intense molecular ion peaks which confirmed the molecular weights of 638 for A and 652 for B. The mass spectra also indicated that some samples contained two other related compounds, of molecular weights 666 and 652.

Fig. 1 presents the mass spectra of A and B; the figures in brackets placed after the  $m/e$  values in the spectrum of A and also in the text are the shifts which the peaks display in the mass spectrum of N-deuteriated A prepared by exchange of A with D<sub>2</sub>O.

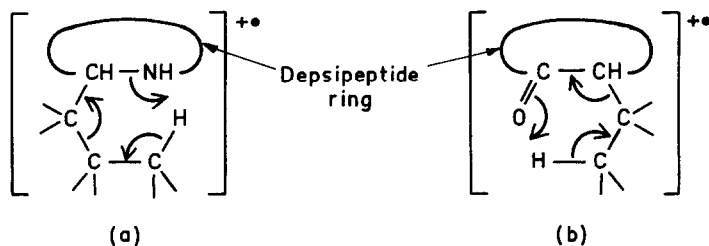
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† For previous descriptions of the mass spectra of peptides and depsipeptides see References (1) and (7) respectively.

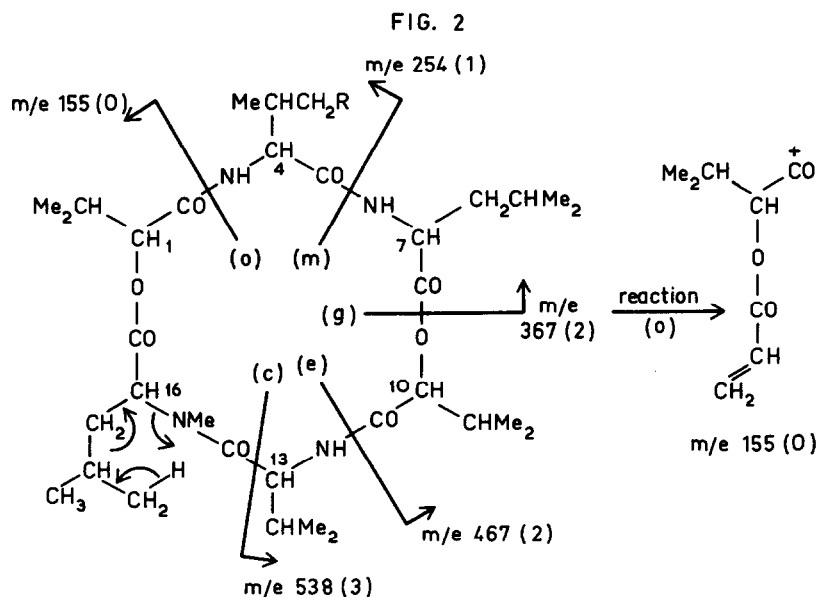
FIG. 1



The M-42 peaks ( $m/e$  596(3) from A,  $m/e$  610 from B) and the M-56 peaks ( $m/e$  582 from A,  $m/e$  596 from B) are due to side-chain fission, probably involving reaction (a) or reaction (b) (cf. References (5) and (6)), e.g.



It is proposed that many important peaks in both spectra are due to reaction (a) at position 7 or position 16, accompanied by homolytic cleavage  $\alpha$  to a carbonyl group (Table 1 and Fig. 2).



$A^{+\bullet}$  (R=H),  $B^{+\bullet}$  (R=CH<sub>3</sub>). The  $m/e$  values refer only to peaks due to A.

TABLE 1

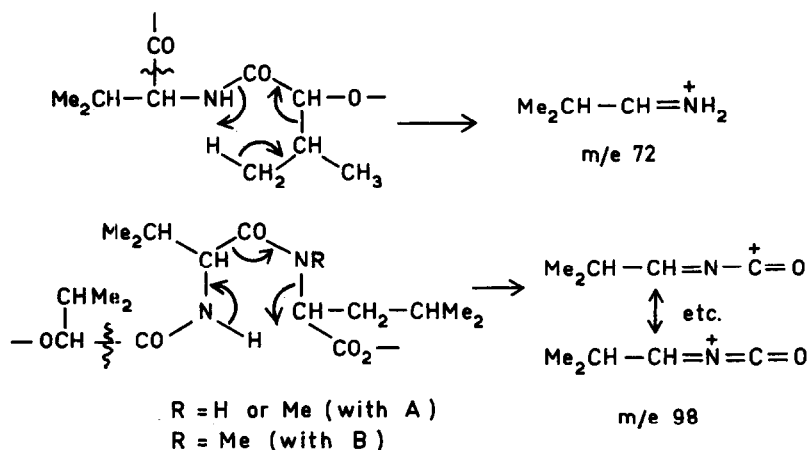
Reaction	Position of reaction (a)	Position of homolytic cleavage	*	Peaks due to A	Peaks due to B
c	16	13-14	-	538(3)	552
d	7	2-3	-	481(1)	481
e	16	11-12	-	467(2)	481
f	7	17-18	-	381(1)	381
g	16	8-9	-	367(2)	381
h	7	2-3	10,13,1	355(1)	-
i	16	11-12	1,4,10	-	341
j <sup>†</sup>	7	2-3	10,13,1	327(1)	327
k <sup>†</sup>	16	11-12	1,4,10	-	313
l	7	14-15	-	254(1)	-
m	16	5-6	-	254(1)	-
n <sup>‡</sup>	7	11-12	-	155(0)	155
o <sup>‡</sup>	16	2-3	-	155(0)	155
p <sup>†‡</sup>	7	11-12	-	127(0)	127
q <sup>†‡</sup>	16	2-3	-	127(0)	127

\* Reaction (a) and homolytic cleavage are preceded by loss of side-chains at the positions shown and ketonization of the enols so formed.

† Reaction (a) and homolytic cleavage are followed by loss of CO.

‡ Metastable peak at  $\frac{127^2}{155}$ .





We are currently examining other depsipeptides by the above methods.

However, these preliminary results demonstrate the important role played by mass spectrometry in structural studies with this class of compound.

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