

²⁵²Cf PLASMA DESORPTION MASS
SPECTROMETRY OF ADENOMYCIN
(C₁₉₋₉₇ SUBSTANCE)

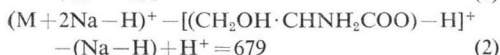
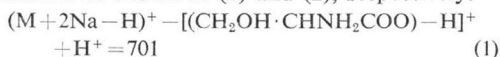
Sir:

Adenomycin¹⁾, an antibiotic produced by *Streptomyces griseoflavus* is effective against a wide range of mycobacteria. The complete structure of adenomycin has been established as that depicted in Fig. 1, which demonstrates that the antibiotic is a new class of adenine nucleoside consisting of D-ribose, (-)-chiro-inositol, L-gulosamine, L-serine and sulfate. Because of its low volatility, molecular weight determination of adenomycin by the usual means utilizing EI, CI and FD mass spectrometries was unsuccessful.

The problem was resolved by the application of ²⁵²Cf plasma desorption mass spectrometry (²⁵²Cf PDMS) to molecular weight determination. This technique has been shown to be a powerful and efficient tool for investigations of natural products chemistry²⁻⁴⁾.

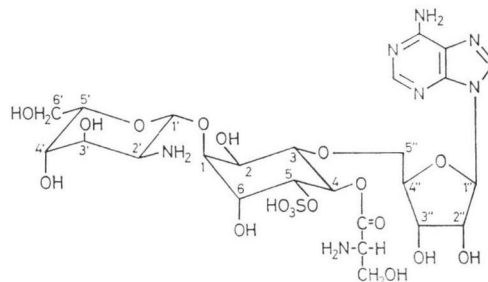
We have determined that the molecular weight of adenomycin is 757.86 by ²⁵²Cf-PDMS. This result gave good agreement with the molecular formula, C₂₅H₃₉N₇O₁₅S (757.68) obtained by elemental analyses of the corresponding dihydrochloride dihydrate. [Calcd. for C₂₅H₃₉N₇O₁₅S·2HCl·2H₂O: C, 34.70; H, 5.80; N, 10.72; O, 36.61; S, 3.77; Cl, 7.95. Found: C, 34.64; H, 5.24; N, 11.31; O, 36.92; S, 3.72; Cl, 8.18].

Determination of molecular weight was based on an analysis of both positive and negative ion mass spectra. The positive ion spectrum in the molecular ion region is shown in Fig. 2. (Spectrum I) A peak at 803 is assigned to (M+2Na-H)⁺, the result of a two-step process involving Na⁺-H⁺ exchange followed by Na⁺ addition. This can occur when [Na⁺] is high as it was in the sample. A weaker peak at 780 is attributed to (M+Na-H)⁺. The peaks at 701 and 679 we believe are the fragment ions possibly derived from loss of serine residue or serine residue plus Na⁺ involving H⁺ exchange followed by H⁺ addition as shown in (1) and (2), respectively.

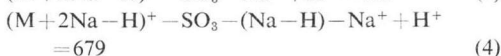
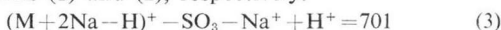


An alternative interpretation is also possible as shown in (3) and (4), however, the presence of a weak peak at 716 which is ascribable to a loss

Fig. 1. The structure of adenomycin.



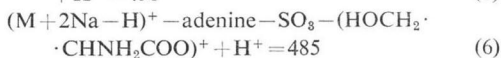
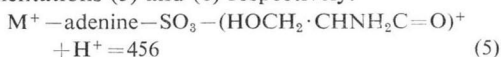
of a part of serine residue (HOCH₂·CHNH₂·C=O)⁺ from (M+2Na-H)⁺ followed by H⁺ addition gave strong support for the fragmentations (1) and (2), respectively.



The negative ion spectrum in the molecular ion region (Spectrum II) shows a dominant peak at 756.9 (isotopically averaged) which we have assigned to (M-H)⁻ and confirms the assignment derived from the positive ion results. We also observed a fragment ion at 670, which is possibly the result of loss of a part of serine residue (OHCH₂·CHNH₂·C=O)⁻ followed by H⁺ addition.

Other fragment ions were also observed in the positive ion spectrum. Spectrum III shows a strong ion peak at 136 due to the adenine residue.

The prominent peaks at 456 and 485 in Spectrum IV are the ions derived by the following fragmentations (5) and (6) respectively.

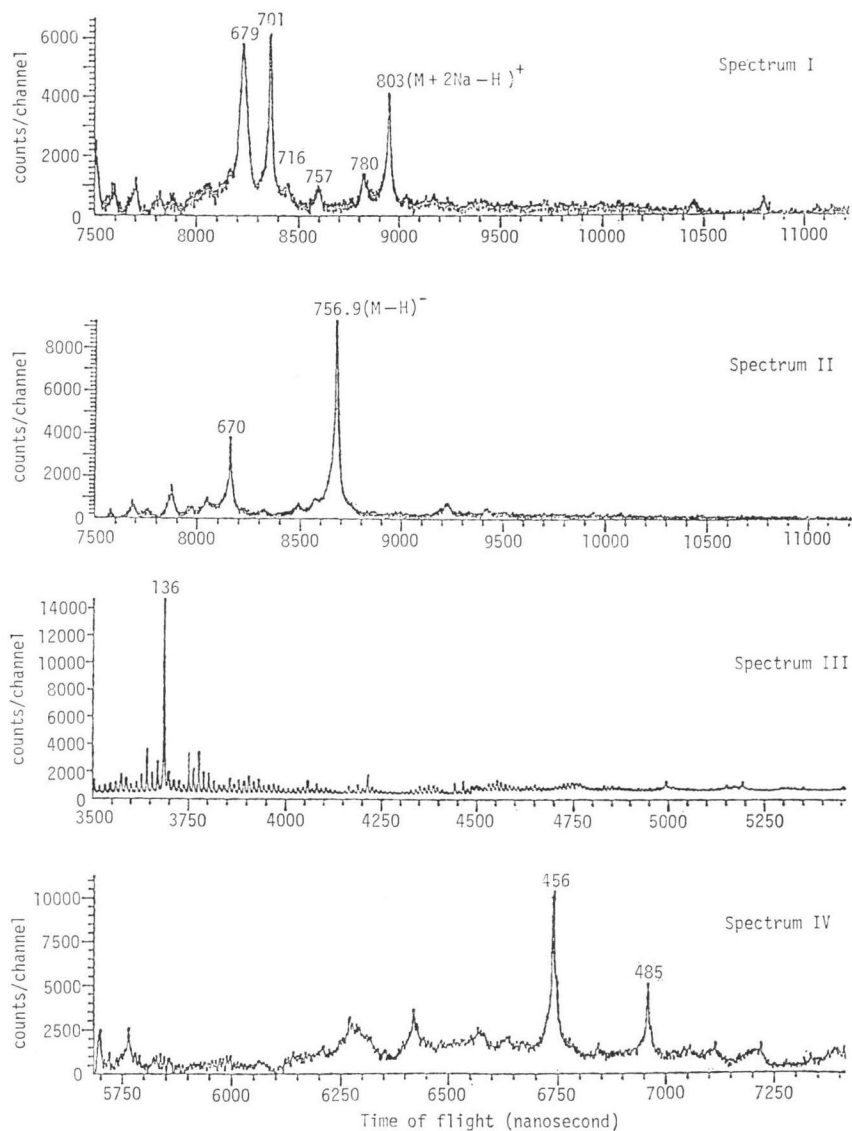


The following results gave strong support for the molecular formula assigned to adenomycin as well as its structure as depicted in Fig. 1.

Acknowledgments

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Fig. 2. The ^{252}Cf plasma desorption mass spectra of adenomycin.

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