is expected to restrict the possible relative orientations of the purine bases. More detailed analysis of the CD spectra of these and other nucleotide species coordinated to Pt(II) may provide better insight into the structure of the Pt-DNA complex which promotes the enhanced CD effect, and these compounds may be of value in theoretical studies of the effect of base stacking or metal binding on the CD spectra of nucleotide species.

Acknowledgments. The authors thank the NIH (GM 20544) for support and Matthey-Bishop, Inc., for a loan of K_2PtCl_4.

References and Notes

(1) Abbreviations used: dien = diethylenetriamine; GC = guanine cytosine; 5′-GMP and 5′-dGMP = 5′-guanosinemonophosphate and the 2′-deoxy analogue, respectively; Guo = guanosine; Pt-DNA = complex formed between *cis*Pt and DNA at low Pt/DNA; and tn = trimethylenediamine.
(2) Rosenberg, B.; Van Camp, L.; Trosko, J. E.; Mansour, V. H. *Nature (London)* **1969**, *222*, 385.
(3) Roberts, J. J.; Thomson, A. J. *Prog. Nucl. Acid Res. Mol. Biol.* **1979**, *22*, 71.
(4) Marzilli, L. G. *Prog. Inorg. Chem.* **1977**, *23*, 255.
(5) Gellert, R. W.; Bau, R. *J. Am. Chem. Soc.* **1975**, *97*, 7379.
(6) Kelman, A. D.; Buchbinder, M. *Biochimie* **1978**, *60*, 893.
(7) Srivastava, R. C.; Froehlich, J.; Eichhorn, G. L. In "Platinum Coordination Compounds in Cancer Chemotherapy", Connonrs, T. A., Roberts, J. J., Eds.; Springer: Heidelberg, 1974; p 75.
(8) Srivastava, R. C.; Froehlich, J.; Eichhorn, G. L. *Biochimie* **1978**, *60*, 879.
(9) Macquet, J. P.; Butour, J. L. *Eur. J. Biochem.* **1978**, *83*, 375.
(10) Goodgame, D. M. L.; Jeeves, I.; Phillips, F. L.; Skapski, A. C. *Biochim. Biophys. Acta* **1975**, *378*, 153.
(11) Bau, R.; Gellert, R. W.; Lehovec, S. M.; Louie, S. *J. Clin. Hematol. Oncol.* **1977**, *7*, 51.
(12) Kistenmacher, T. J.; Chiang, C. C.; Chalilpoyil, P.; Marzilli, L. G. *J. Am. Chem. Soc.* **1979**, *101*, 1143.
(13) Kistenmacher, T. J.; Chiang, C. C.; Chalilpoyil, P.; Marzilli, L. G. *Biochem. Biophys. Res. Commun.* **1978**, *84*, 70.
(14) Melanson, R.; Rochon, F. D. *Can. J. Chem.* **1979**, *57*, 57.
(15) Rifkind, J. M.; Eichhorn, G. L. *J. Am. Chem. Soc.* **1972**, *94*, 6526.
(16) Gellert, M.; Lipsett, M. N.; Davies, D. R. *Proc. Natl. Acad. Sci. U.S.A.* **1962**, *48*, 2013.
(17) Yang, J. T.; Samejima, T. *Prog. Nucl. Acid Res. Mol. Biol.* **1969**, *9*, 223.

Luigi G. Marzilli,* Purush Chalilpoyil
Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218
Received August 2, 1979

^{252}Cf Plasma Desorption Mass Spectrometry of Palytoxin

Sir:

Palytoxin is the most powerful toxin among those obtained from marine animals.[1] There has been considerable interest in elucidating the structure of this molecule because of its unusual physiological and molecular properties.[2,3] Despite its high molecular weight (estimated to be ~3300),[4] there do not appear to be any repeating units of sugars and amino acids and its toxicity can be markedly reduced by subtle changes in its chemical structure. Recently, larger quantities of highly purified fractions of the toxin have become available and studies on structural details of pieces of the molecule are now being carried out using this material.[5,6] Previous attempts to determine the molecular weight by field desorption were hampered by sample purity problems.[7] Because of its high mass, low volatility, and thermal instability, this molecule represents one of the most difficult problems ever encountered for a mass spectrometric measurement of a natural product. We report here the molecular weight determination of highly purified palytoxin (M_1) by ^{252}Cf plasma desorption mass spectrometry (^{252}Cf PDMS). We also report molecular weight determinations for *N*-acetylpalytoxin (M_2) and *N*-acetylperhydropalytoxin (M_3).

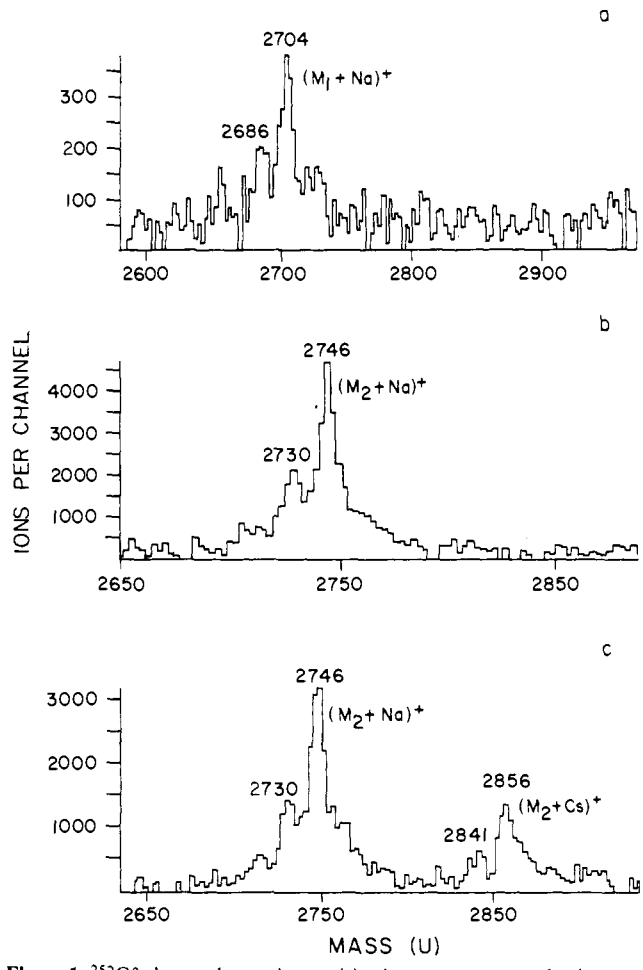

Figure 1. ^{252}Cf plasma desorption positive ion mass spectra of palytoxin and derivatives: (a) palytoxin, T = 10 000 s; (b) *N*-acetylpalytoxin, T = 112 000 s; (c) *N*-acetylpalytoxin deposited over a film of CsI, T = 50 000 s.

Details of the ^{252}Cf PDMS method are given in an earlier paper.[8] The system was optimized for high mass ion analysis by reducing the flight path of the time-of-flight mass spectrometer to 45 cm and operating the CEMA electron multiplier detectors at high gain for improved detection efficiency of high-mass ions. Palytoxin was isolated from *palythoa tuberculosa* and purified according to a new method published elsewhere.[5] Acetylation of palytoxin was carried out with *p*-nitrophenyl acetate in water containing a trace amount of pyridine giving *N*-acetylpalytoxin,[9] a species with considerably reduced toxicity. *N*-acetylperhydropalytoxin was formed by catalytic hydrogenation of the monoacetate with platinum oxide in aqueous ethanol. Thin deposits of palytoxin (~10 μg/cm^2) were prepared by direct evaporation of a 2-propanol-methanol-water solution onto a Ni foil (10^{-3} mm thick). More uniform deposits of the two derivatives which were much less toxic were made by an electrospray method[10] and were of an equivalent thickness. The samples were irradiated with a ^{252}Cf source giving a fission fragment (FF) flux in the samples of 2500 FF/(cm^2 s) for periods of up to 31 h. The mass region covered was from 0 to 5000 u. Positive and negative ion mass spectra were recorded, but only the positive ion spectra gave significant results.

Figure 1a shows part of the positive ion spectrum of palytoxin in the region of M = 2650-2900 u where a significant peak was detected at M = 2704 u. There was also evidence of a second smaller peak at M = 2686 u. No peaks were observed above M = 2900 u. The lower mass region showed a complex pattern of fragment ions extending to ~1600 u with few prominent lines. Figure 1b shows the spectrum obtained for

0002-7863/80/1502-0875$01.00/0

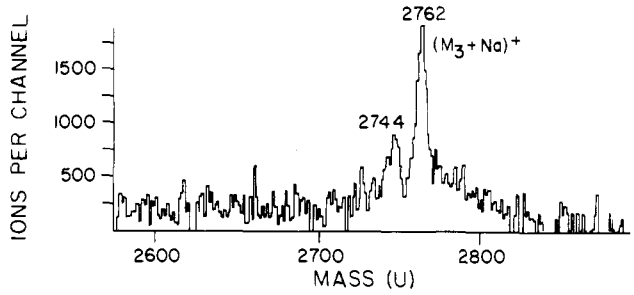

Figure 2. ^{252}Cf plasma desorption positive ion mass spectrum of *N*-acetylperhydropalytoxin, $T = 54\,000$ s.

N-acetylpalytoxin in the same mass region. A prominent peak was observed at M = 2746 u and a smaller peak at 2730 u. Again, no peaks were observed above M = 2900 u. The mass increase of 42 u for the *N*-acetyl derivitive is consistent with the addition of an *N*-acetyl group to palytoxin. If these ions comprise the intact molecule, they are most likely adducts of the form $(M + Na)^+$. To test this, we performed a second experiment on the *N*-acetylpalytoxin where a thin film of the material was electrosprayed over a layer of CsI. When the double layer is activated by a fission fragment, Cs^+ ions are released from the bottom layer, rapidly diffuse through the fission track, percolate through the molecules in the upper layer, and have some probability of forming ion-dipole complexes of the form $(M + Cs)^+$. The result of this experiment is shown in Figure 1c. An additional peak at M = 2856 u is now observed whose mass is 110 u higher than the primary peak. This is precisely the (Cs − Na) mass difference. Thus, the identification of the peaks in the previous spectra as $(M + Na)^+$ adducts is verified. Although the possibility cannot be ruled out that these are fragment ions of a larger molecule, it seems unlikely that this is the case. There is no evidence of higher mass peaks down to the level of 5% of the intensity of the peaks observed. The molecule undoubtedly has multiple sites where an alkali metal ion could attach and the probability is very small that fragmentation would yield a single Na^+-containing fragment with a unique mass independent of the Na-attachment site. From the results of four independent measurements, the molecular weight of the $(M + Na)^+$ adduct of *N*-acetylpalytoxin is 2746.1 ± 0.35 u. The molecular weight of *N*-acetylpalytoxin is, therefore, 2723.1 ± 0.35 u (M_2) and palytoxin, 2681.1 ± 0.35 u (M_1). Since the ^{13}C satellites were not resolved, these masses are isotopically averaged values (C = 12.011 u).[11]

The positive ion spectrum of *N*-acetylperhydropalytoxin is shown in Figure 2. A significant peak is observed at M = 2762 and a smaller peak at 2744 u. Assigning the more intense peak to the type $(M + Na)^+$ gives M = 2739.4 ± 0.4 u (M_3). The mass increase as a result of hydrogenation of *N*-acetylpalytoxin is 16.3 ± 0.6 u suggesting that the parent molecule contains eight double bonds. In all of these samples, there is evidence of a second component of palytoxin with a mass 16-18 u lower than the principal component.[12]

Acknowledgments. We acknowledge the contributions of C. J. McNeal and Dr. S. Hosozawa to these experiments. This work was supported by the National Institutes of Health (GM-26096) (R.D.M.).

References and Notes

(1) R. E. Moore and P. J. Scheuer, *Science*, **172**, 495 (1971).
(2) R. E. Moore, R. F. Dietrich, B. Hatton, T. Higa, and P. J. Scheurer, *J. Org. Chem.*, **40**, 540 (1975).
(3) Pharmacological studies on palytoxin were carried out by cooperation with Shibata's group using frog spinal cord (unpublished work). After injection of the toxin, the facilitation of ventral root reflex was observed in 10 min, and in another additional 10 min this reflex was essentially inhibited. The effect was diminished in high concentrations of Ca^{2+} ions. Therefore, its action against frog spinal cord may be caused by the opening of the Na^+ channel.
(4) R. E. Moore, F. X. Woolard, M. Y. Sheikh, and P. J. Scheuer, *J. Am. Chem. Soc.*, **100**, 7758 (1978).
(5) This work was reported at the Second International Symposium on Marine Natural Products, Sorrento, 1978; Y. Hirata, D. Uemura, K. Ueda, and S. Takano, *Pure Appl. Chem.*, in press.
(6) Presented at the International Conference on Natural Substances of Biological Interest from the Pacific Area, Noumea, Nouvelle Caledonie, 1979.
(7) D. Brent, private communication.
(8) R. D. Macfarlane and D. F. Torgerson, *Int. J. Mass Spectrom., Ion Phys.*, **21**, 81 (1976).
(9) This compound was obtained in quantitative yield from palytoxin itself. Except for acetylation of the primary amino group, there is no characteristic change between the structures of *N*-acetylpalytoxin and palytoxin itself as determined by the similarities of the ^{13}C and ^1H NMR species.
(10) C. J. McNeal, R. D. Macfarlane, and E. L. Thurston, *Anal. Chem.*, **51**, 2036 (1979).
(11) New results recently obtained from chemical degradation and elemental analysis show that the most plausible molecule formula of palytoxin is $C_{121}H_{207-209}N_3O_{61}$.
(12) We have also observed this by means of high pressure TLC and LC.

R. D. Macfarlane*
Department of Chemistry, Texas A & M University
College Station, Texas 77843

Daisuke Uemura
Chemical Research Laboratory, Faculty of Liberal Arts
Shizuoka University, Ohya, Shizuoka 422, Japan

Katsuhiro Ueda
Department of General Education
University of Ryukyus, Naha 903, Japan

Yoshimasa Hirata*
Faculty of Pharmacy, Meijo University
Tempaku, Nagoya 468 Japan
Received October 4, 1979

Electrically Conductive Polyimide Films Containing Palladium Coordination Complexes

Sir:

Polymers which conduct an electric current have received considerable attention in the recent chemical literature. Although a few polymeric systems such as $(SN)_x$,[1] polyacetylene,[2] and poly(*p*-phenylene)[3] have conducting properties when complexed with electron donors or accepters, the majority do not. The incorporation of conductive fillers into insulative polymers is one of the most common methods for imparting electrical conductivity. To date these fillers have been at rather high concentrations and primarily particulate in nature such as metal and carbon fibers.[4] The doping of polymers with dissolved metal salts for this purpose has received little attention. Success has been marginal where this technique has been applied (e.g., little enhancement in both surface and volume electrical conductivity).[5-8] It should be noted, however, that 20 years ago there was a brief report[9] regarding the incorporation of bis(acetylacetonato)copper(II) into a polyimide which resulted in a significant decrease in volume electrical resistivity ($\sim 10^{12}$ Ω cm). No other reports of this study have appeared in the open literature. We communicate a significant success in this area by reporting the production of palladium-containing polyimide films which exhibit surface and volume resistivities approximately ten orders of magnitude lower than that measured for the polymer alone.

The polyimide precursors selected for this study were 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride (BTDA, I) and 4,4′-oxydianiline (ODA, II). Best results were

0002-7863/80/1502-0876$01.00/0