Desorption Mass Spectrometry of Olestra

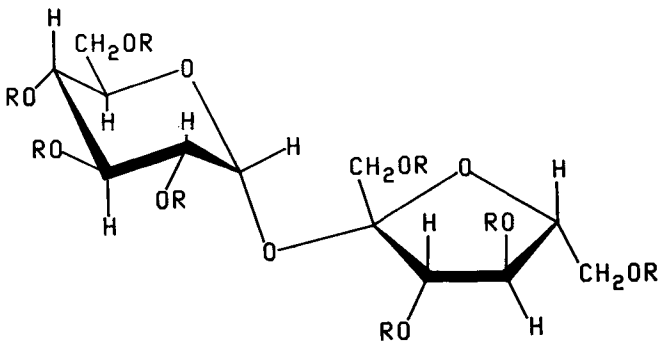
R.A. Sanders[a,*], D.R. Gardner[a], M.P. Lacey[b] and T. Keough[b]

[a]The Procter and Gamble Co., Winton Hill Technical Center, Cincinnati, Ohio 45224 and [b]The Procter and Gamble Co., Miami Valley Laboratories, Cincinnati, Ohio 45239-8707

Field desorption (FD), fast atom bombardment (FAB) and plasma desorption (PD) mass spectrometry have been used for the characterization of olestra, a mixture of octa-, hepta- and hexaesters of sucrose formed by reaction of sucrose with long-chain fatty acids (C_{12}–C_{18}). Most previous applications of desorption ionization mass spectrometry have involved polar compounds; however, the relatively low-polarity olestra is also amenable to these techniques with proper sample preparation. Field desorption provides molecular weight information, but the transience of the signals limits the usefulness for observing fragmentation and measuring ester distributions. In addition, FD may not be sensitive enough to allow characterization of fractions isolated from analytical high-performance liquid chromatography (HPLC) columns. Fast atom bombardment produces longer-lasting signals, which permit characterization of components over a wide mass range. However, signal-to-noise fluctuates substantially, depending on analyte solubility in the matrix, making the characterization of partial esters collected from HPLC uncertain and difficult. Plasma desorption mass spectrometry is the easiest and most sensitive technique for olestra characterization but provides the lowest mass resolution. Because it requires no more than a few μg of material, it is effective for the characterization of HPLC fractions. Furthermore, it is the only method, of the three investigated, that allows detection of intact dimeric species having molecular masses in the 3,000 to 5,000 dalton range.

KEY WORDS: DMS, fast atom bombardment, field desorption, heated lipids, lipids, mass spectrometry, olestra, plasma desorption.

Olestra, formerly called sucrose polyester, is a mixture of octa-, hepta- and hexaesters of sucrose, formed by reaction of sucrose with long-chain fatty acids. The structure of the octaester component of olestra is shown in Scheme 1 where R = any long-chain fatty acyl group in the range C_{12} to C_{18}. Olestra possesses functional properties similar to triacylglycerols when used in food products. However, because olestra is neither metabolized (1) nor absorbed (2), it makes no caloric contribution to the diet.



SCHEME 1

Rapid and reliable analytical methods are needed to identify individual polyesters in olestra and to provide qualitative data concerning the detailed composition of olestra. Mass spectrometry provides a wealth of information about the structures of traditional fats and oils (3,4). For example, C_{16}–C_{18} triacylglycerols may be analyzed, without derivatization, by means of a solids probe and electron (EI) (5) or chemical ionization (CI) (6). EI provides low-abundance molecular ions and intense fragments such as RCO^+, $(M-RCO_2)^+$ and others that establish unambiguously the fatty acid composition of the molecule (7). Ammonia CI (8) produces abundant MNH_4^+ adduct ions that are particularly useful for determining the molecular weights of triacylglycerol components in mixtures (9). Unfortunately, sucrose octa-, hepta- and hexaesters are not volatile enough to allow characterization by EI or CI methods. Desorption ionization techniques (10–13) would appear to be better suited for this application because they eliminate sample volatility requirements altogether. The goal of this work was to determine the utility of various desorption ionization methods, particularly fast atom bombardment (FAB) and plasma desorption (PD), for the characterization of olestra standards, mixtures and high-performance liquid chromatography (HPLC) isolates. The types of structural information obtainable as well as relative sensitivities and ease of operation were evaluated. Some field desorption (FD) work, which was accomplished in 1977 (14), is also included in this paper, although it does not reflect the capabilities of FD with today's more sensitive instruments (it is included for comparison purposes only).

EXPERIMENTAL PROCEDURES

High-performance liquid chromatography (HPLC). Normal-phase HPLC was used to separate olestra components according to the number of esterified sites. A Hewlett-Packard (Palo Alto, CA) 1090 HPLC system was used with a Zorbax Reliance (MAC-MOD Analytical Inc., Chadds Ford, PA), 80 mm × 4 mm, 5-μm silica column and a variable volume injector (20-μL injections were made). Eluting solvent was a binary mixture of methyl-*t*-butyl ether (MTBE) in hexane (both Burdick and Jackson, HPLC-grade, Muskegon, MI) delivered at a flow rate of 1.5 mL/min in a stepwise gradient as follows: 4.8% MTBE (0–5 min), 16% MTBE (5–8 min), 25% MTBE (8–10 min), 50% MTBE (10–12 min) and 100% MTBE (12–15 min). The detector was a Varex L/LSD (light-scattering detector) Rockville, MD, operated at 75°C.

Size-exclusion HPLC conditions, used to isolate the olestra dimer, are described elsewhere (15).

Mass spectrometry. Field desorption (16,17) mass spectra were obtained on a Kratos MS-5076 mass spectrometer at an ion accelerating voltage of 8 kV (Kratos Analytical, Ramsey, NJ). Olestra samples were loaded onto high-

*To whom correspondence should be addressed at The Procter and Gamble Co., Winton Hill Technical Center, 6071 Center Hill Road, Cincinnati, Ohio 45224.

temperature activated, benzonitrile-coated, 10-μm tungsten wire emitters (18) from 10–30 mg/mL chloroform solutions by the dipping technique (19). Maximum signals in the molecular ion regions were obtained with emitter heating currents (20) between 12 and 15 mA. The FD spectra (Fig. 1), which correspond to single scans, were output to an ultraviolet (UV) strip-chart recorder with timing marks calibrated previously against phosphazine reference ions obtained by EI.

Fast atom bombardment (21) mass spectra were acquired on a previously described (22) VG ZAB-2F mass spectrometer (Fisons Instruments, Danvers, MA) with an ion accelerating voltage between 4 and 6 kV. Of the FAB matrices (23,24) tried, including glycerol and thioglycerol, the most consistent results were obtained from a 5:1 mixture of dithiothreitol:dithioerythritol (DTT/DTE) containing about 1 mg/mL of NaI, which was added to facilitate analyte cationization (22). The olestra concentrations were

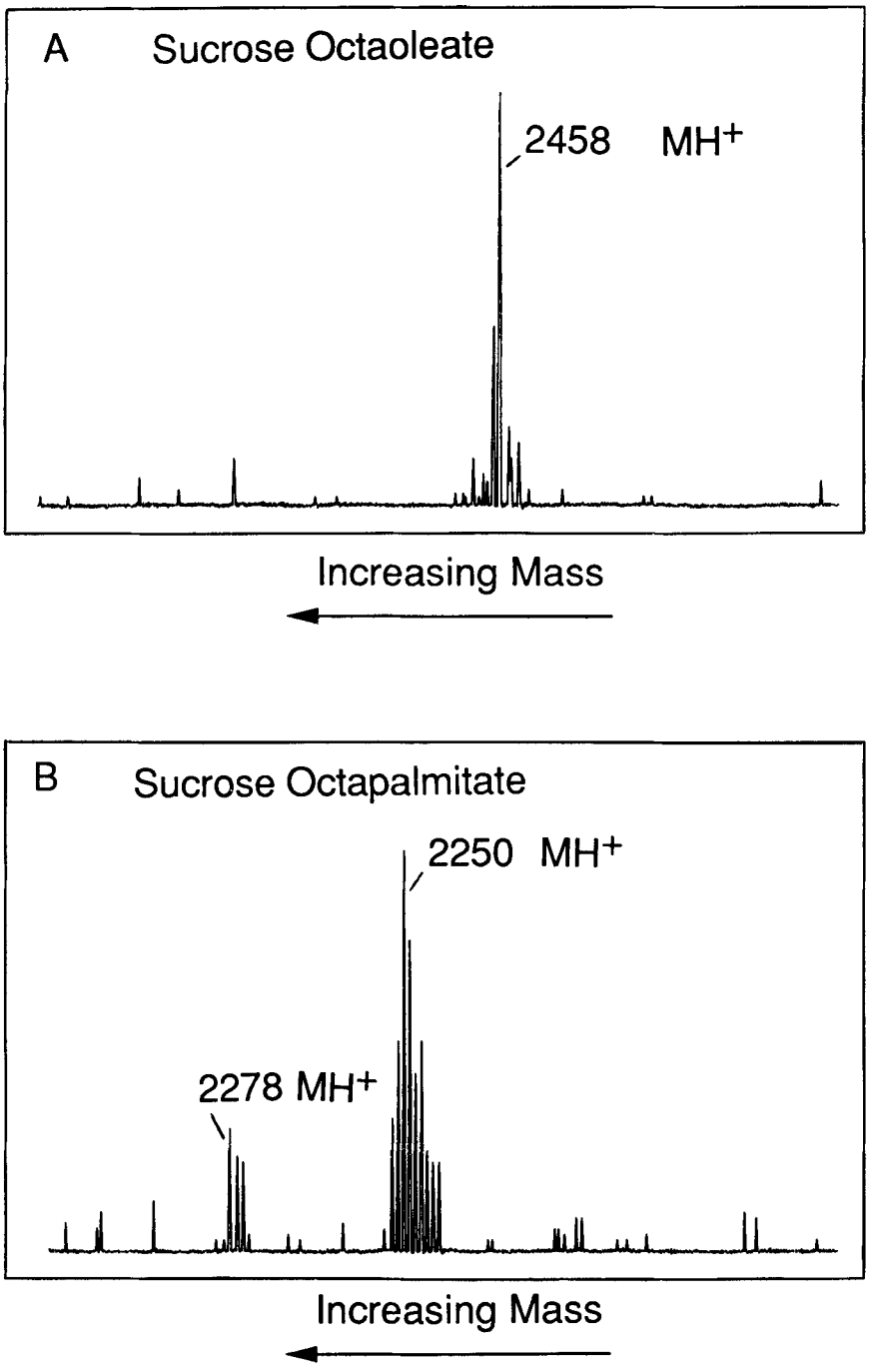


FIG. 1. Field desorption mass spectra in the molecular ion region of (A) sucrose octaoleate and (B) sucrose octapalmitate.

also about 1 mg/mL. Since completing the FAB portion of this study, we have learned that a 1:1 mixture of 2-hydroxyethyl disulfide:thioglycerol may be an even better FAB matrix for nonpolar molecules such as olestra. Some results, prior to acquisition of computerized signal averaging capabilities, were obtained as single scans across the molecular ion regions. These scans were mass calibrated against a Hall probe and were output to a Honeywell model SE-6150 UV recorder (EMI, Ltd., Feltham, England). The spectra (Fig. 2) of sucrose

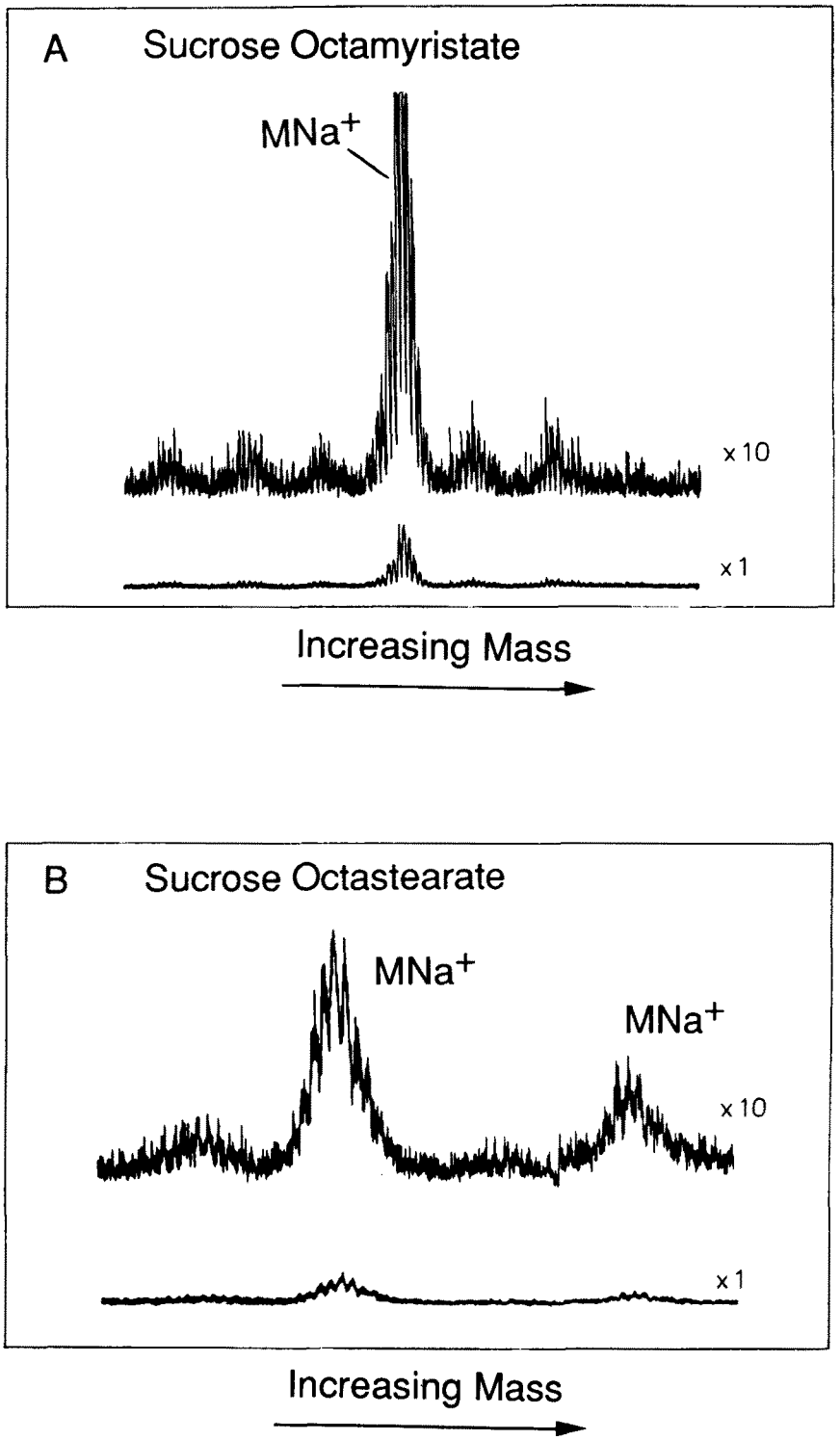


FIG. 2. Fast atom bombardment mass spectra in the molecular ion region of (A) sucrose octamyristate and (B) sucrose octastearate.

octamyristate and sucrose octastearate were obtained in this fashion with approximately unit-mass resolution and can be compared directly to the FD spectra. Subsequent results, particularly from HPLC fractions, were acquired with a VG 11-250J data acquisition system that allows signal averaging over a portion of the mass range. The data shown in Figure 3 were obtained with computerized signal averaging at low mass resolution ($M/\Delta M = 500$). CsI cluster ions, observed with identical scan conditions, were used for mass calibration.

Plasma desorption (25,26) mass spectra (Figs. 4–8) were obtained on a BioIon 20 linear time-of-flight mass spectrometer equipped with a 10-μCi californium-252 source. All samples were analyzed from aluminum foils coated with a nitrocellulose film (27) by the electrospray method (28). The nitrocellulose substrate was then coated with 5 nmols of NaI by evaporation from a 1:1 water:ethanol solution (except for the sample whose spectrum is given in Figure 4A, which was obtained without NaI for comparison purposes). Finally, no more than 10 nmols of olestra were deposited onto the NaI-containing foil by evaporation from a 70:30 hexane:benzene solution. This particular solvent system was used to minimize disruption of the nitrocellulose/NaI layer. During analysis, samples were bombarded with about 1800 fission fragments per second. Data acquisition times of about 20 min (two million fission fragment events) were adequate for analyses of major components.

RESULTS AND DISCUSSION

Field desorption. A field desorption mass spectrum spanning the molecular ion region of sucrose octaoleate is shown in Figure 1A. From the known elemental composition of this molecule, $C_{156}H_{278}O_{19}$, the calculated isotopic distribution exhibits a maximum abundance at 2457 daltons. The experimentally observed base peak at 2458 daltons, corresponding to the protonated molecule MH^+, confirms the molecular mass of this species. The absence of any significant ions at masses immediately above or below the expected molecular ions confirms the purity of the fatty acid used as a starting material in this synthesis. An FD spectrum of sucrose octapalmitate, $C_{140}H_{262}O_{19}$, given in Figure 1B, also reveals the expected protonated molecule at 2250 daltons (corresponding to the most abundant ion in the isotopic distribution). However, a cluster of peaks at higher mass is observed due to a stearic acid impurity in the starting palmitic acid. Subsequent fatty acid composition analysis by gas chromatography (GC) confirmed that the palmitic acid contained 4.6% stearic acid. The spectrum illustrates the important effect that the composition of the starting fatty acid has on the final olestra product distribution. Because there are eight sites available for incorporating the impurity, about 37% of the octaester contains one stearate group.

The spectra in Figure 1 reveal sufficient dynamic resolution ($M/\Delta M = 5000$) and absence of chemical noise to allow unambiguous assignment of molecular weights. Because the primary interest at the time of this work was molecular weight determination, and because the transient nature of the signal made it difficult to acquire representative scans over a wide mass range, fragmentation at lower mass was not investigated. Furthermore, no attempt was made to determine ester distributions of complex olestra mixtures. Finally, attempts to obtain FD spectra on low μg quantities of sucrose octaesters, isolated by HPLC, were unsuccessful even at lower mass resolution ($M/\Delta M = 1000$). Again, it should be reiterated that these FD data were obtained 14 yr ago with instrumentation that was state-of-the-art at that time. The sensitivity of present-day instruments is expected to be considerably improved due to better ion source design, better detectors and computer-based signal averaging.

Fast atom bombardment. Fast atom bombardment of olestra was tried from a variety of matrices. Unlike in FD, intact molecular ions were not detected. This indicates that the MH^+ ions produced by FAB are unstable and fragment extensively, mainly by cleavage of the glycosidic bond (data not shown). However, after addition of NaI, the resulting MNa^+ molecular ions are stable and can be used for molecular weight determination.

Thioglycerol doped with NaI was a successful matrix for olestra characterization. However, DTT/DTE was more persistent and more generally applicable to sodium cationization for the wide variety of alkyl chainlengths and degrees of carbon-carbon unsaturation encountered in typical samples. Even so, quite a disparity in sensitivity was observed as illustrated in Figure 2. Sucrose octamyristate (Fig. 2A) produced a single-scan spectrum having a comparable signal-to-noise ratio to the FD results shown in Figure 1. As expected, the monoisotopic MNa^+ ion was observed at *m/z* 2047, 23 daltons greater than that calculated based on the elemental composition ($C_{124}H_{230}O_{19}$) of sucrose octamyristate. Sucrose octastearate (Fig. 2B) required lower mass resolution to achieve usable signals. A higher-molecular-weight impurity, perhaps due to a small amount of arachidic acid in the stearic acid used in the synthesis, is observed 28 daltons above the octastearate MNa^+ ion.

A major advantage of FAB relative to FD is that the FAB-generated signals are persistent, allowing signal averaging for improved detection limits. This is particularly important when olestra is synthesized from a complex mixture of fatty acids because the resulting molecular ions are spread over a large number of masses, reducing the intensity at any single mass and substantially increasing the detection limit. The problem is further aggravated when analyzing small quantities of materials such as HPLC isolates. Figure 3A shows the low-resolution, signal-averaged FAB spectrum of a sucrose octaester isolated from HPLC. This component was isolated from a mixture of sucrose polyesters made from soybean oil fatty acids, mainly C_{18} fatty acids with 0, 1 and 2 carbon-carbon double bonds and some saturated C_{16} fatty acid. The spectrum was obtained by summing repetitive, linear magnet scans over the indicated mass range and was calibrated against CsI cluster ions generated in a separate experiment. This type of wide mass scan survey analysis was used initially to quickly locate signals within the mass spectrum and to determine their approximate *m/z* values. The spectrum illustrates the signal-to-noise ratio achievable by averaging about 10 low-resolution scans. It also reveals a distribution of octaesters, some containing 8 C_{18}-fatty acids, some with 7 C_{18}- and 1 C_{16}-fatty acids, and some with 6 C_{18}- and 2 C_{16}-fatty acids. Each envelope of ions is fairly broad (full-width half maximum = 12 daltons) because the starting fatty acids contained some unsaturation. Higher-mass

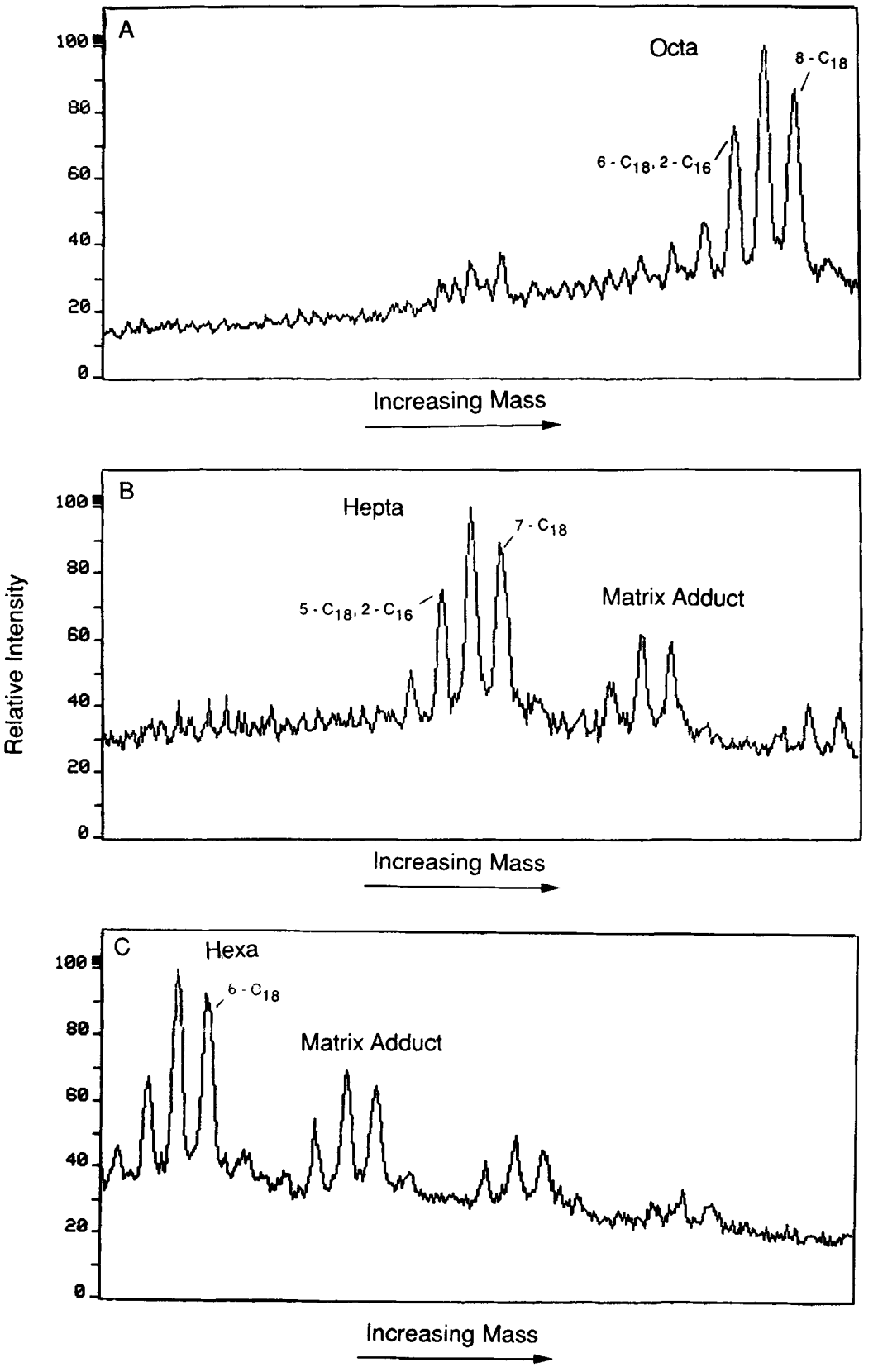


FIG. 3. Low-resolution, signal-averaged FAB mass spectra of (A) the octaester, (B) the heptaester and (C) the hexaester HPLC fractions of an olestra sample prepared from soybean oil fatty acids.

peaks are also evident in the spectrum (not shown) due to matrix adduction with the octaester components. Lower-mass fragment ions, in the 1200 dalton region, were observed in the full-scan spectrum (not shown) and will be discussed with the plasma desorption mass spectrometry (PDMS) results below. Figure 3B displays a similar FAB spectrum for sucrose heptaester fraction isolated from the same HPLC analysis. Again, sodium cationization produces parent ion signals which define the ester content of the fraction. Matrix adduct ions and small octaester parent ions are also evident in the higher-mass region of the spectrum. Figure 3C displays a similar spectrum of a sucrose hexaester isolated from this analysis. Penta- and tetraesters, present in olestra at levels of <1%, have also been successfully screened in this fashion.

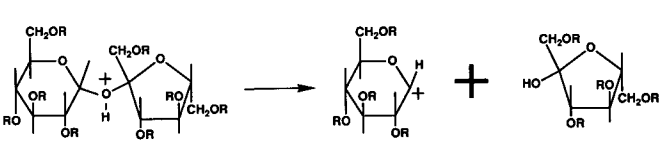
Plasma desorption. Despite successful FAB identification of olestra HPLC fractions, there were several reasons to pursue PDMS as an alternative approach. First, species with very high molecular weights had been observed in the size-exclusion HPLC chromatograms of olestra that had been used in frying applications. They were suspected to be olestra dimers, analogous to those formed in triacylglycerol frying fat (29–32), but FAB produced no ionization in the appropriate mass range. Second, FAB often produced highly unstable signals, especially with olestra samples having fully saturated fatty acid chains. Third, significant variations in FAB sensitivity were observed between olestra samples with different fatty acid compositions. Fourth, FAB instrumentation could not be readily automated and was labor-intensive. Plasma desorption offered viable solutions to all of these problems.

A PD mass spectrum of a mixture of sucrose polylinoleates, with molecular weights spanning the 1900–2600 region, is shown in Figure 4A. The MH^+ ions produced by PDMS are unstable and quantitatively decompose producing the abundant lower-mass fragment ions observed at *m/z* 954 and 1214. Obviously, spectra of this nature provide no direct information on the molecular weights of individual olestra components or on the composition of complex olestra mixtures. However, as shown in Figure 4B, molecular ions can be obtained from PDMS by simply loading the olestra onto nitrocellulose foils that have been previously coated with 5 nmols of NaI. This procedure facilitates the formation of stable MNa^+ molecular ions.

A PD mass spectrum of sucrose polylaurate is shown in Figure 5A. The average molecular weight of the octaester, calculated from isotopically averaged elemental masses (C = 12.011, H = 1.0079, O = 15.9994), is 1801 daltons, and the MNa^+ ion observed at *m/z* 1824 clearly confirms this value. The parent ion peak width is quite narrow, indicating that a pure, single alkyl chainlength fatty acid was used in the synthesis (contrast this result to that obtained from an octaester with a mixed fatty acid composition as shown in Fig. 5B). The spectrum also exhibits a relatively weak response at *m/z* 1641, which corresponds to the MNa^+ parent ion of a heptaester impurity contained in the sample (calculated mass of MNa^+ = 1641 daltons). The mass-measurement accuracy typically achieved with the BioIon PD mass spectrometer is ±0.1%, which is easily good enough to distinguish between the MNa^+ parent ion of a heptaester and either of the potential fatty acid fragment ions produced from the ionized octaester, *i.e.*, the ($MNa^+ - C_{11}H_{23}CO_2H$) ion with a calculated mass of 1624 daltons and the ($MH^+ - C_{11}H_{23}CO_2H$) ion with a calculated mass of 1602 daltons. This result, and results from purified octaesters (not shown), establish that fatty acid fragmentation does not occur to a significant extent in the PD mass spectra of olestra components. Therefore, these spectra can be used to gain qualitative insight into ester distributions of complex olestra mixtures.

The PD mass spectrum of olestra made from hydrogenated soybean oil is shown in Figure 5B. The sample consists primarily of octaesters, a small amount of heptaesters and traces of hexaester, and the spectrum qualitatively reflects this composition. The spectrum also provides insight into the distribution of fatty acids used to synthesize this particular sample. Examination of the octa-C_{18} region (*m/z* 2400–2600) reveals several partially resolved peaks. The peak centered at 2489 daltons is clearly lower in mass than calculated for fully saturated sucrose octastearate (MNa^+ = 2497 daltons). This results because a distribution of fatty acids, containing 0, 1 and 2 carbon-carbon double bonds, was used in the synthesis. The signal at about 2463 daltons corresponds to the isomers having seven C_{18}-chains and one C_{16}-chain. Comparison with the same mass region of the corresponding FAB spectrum, Figure 3A, reveals that similar information is available from both the FAB and PD methods; however, FAB provides superior mass resolution even when the magnetic sector instrumentation was operated under low-resolution conditions. On the other hand, the PD spectra are free from matrix adducts, span the entire mass range in each experiment and can be acquired unattended, with the instrument fully automated.

The main mode of fragmentation in the PD mass spectra involves cleavage of the protonated molecule at the glycosidic bond, with charge retention occurring on either half of the original sucrose molecule as was previously observed in the FABMS analysis of sucrose tri- and tetraesters isolated from *Nicotiana glutinosa* (R = C_2 – C_9) (33). One of the possible fragmentation paths is shown in Equation [1]. This process is analytically quite useful because it allows distinction of particular isomers of incompletely esterified olestra. For instance, the olestra sample synthesized with a mixture of C_{12}, C_{14}, C_{16} and C_{18} fatty acids was quite complex. Spectra obtained from two chromatographically resolved HPLC fractions, both hexaesters, are shown in Figure 6. Both spectra exhibit the same complex distribution of MNa^+ molecular ions. The broad distribution of parent ion masses is not surprising given the distribution of starting fatty acids. The lowest-weight member of the distribution, sucrose hexalaurate, occurs at *m/z* 1459, while the highest-weight member, sucrose hexastearate, occurs at *m/z* 1964. Interestingly, Figure 6A reveals a single distribution of fragment ions in the *m/z* 700–900 region. This is consistent with a relatively pure symmetrical hexaester having three fatty acids (R's) on each of the rings. For this symmetrical structure, the range of fragment ion *m/z* values is from



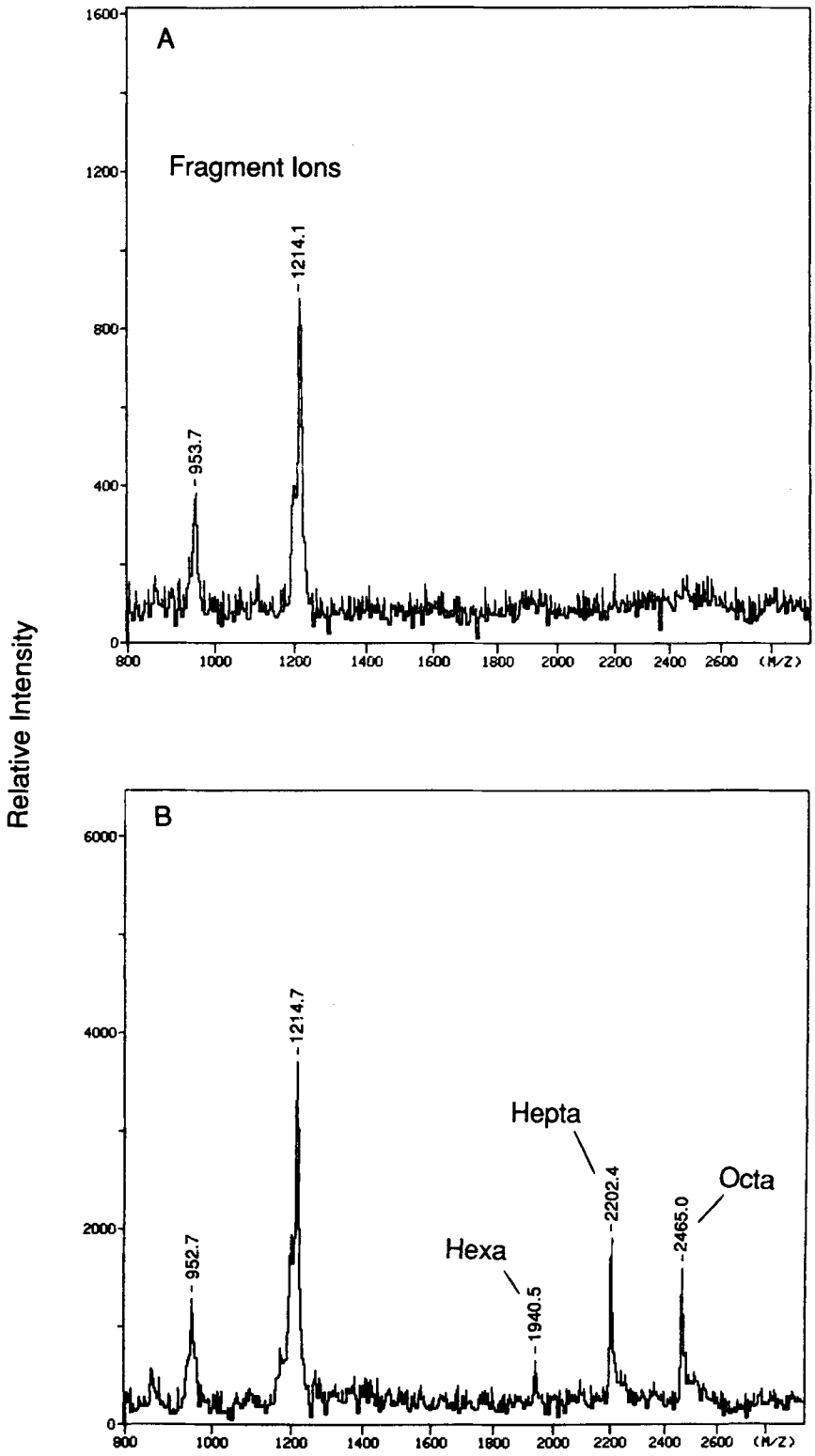


FIG. 4. Plasma desorption mass spectra of a mixture of sucrose polylinoleates from (A) a nitrocellulose foil and (B) a NaI-containing nitrocellulose foil.

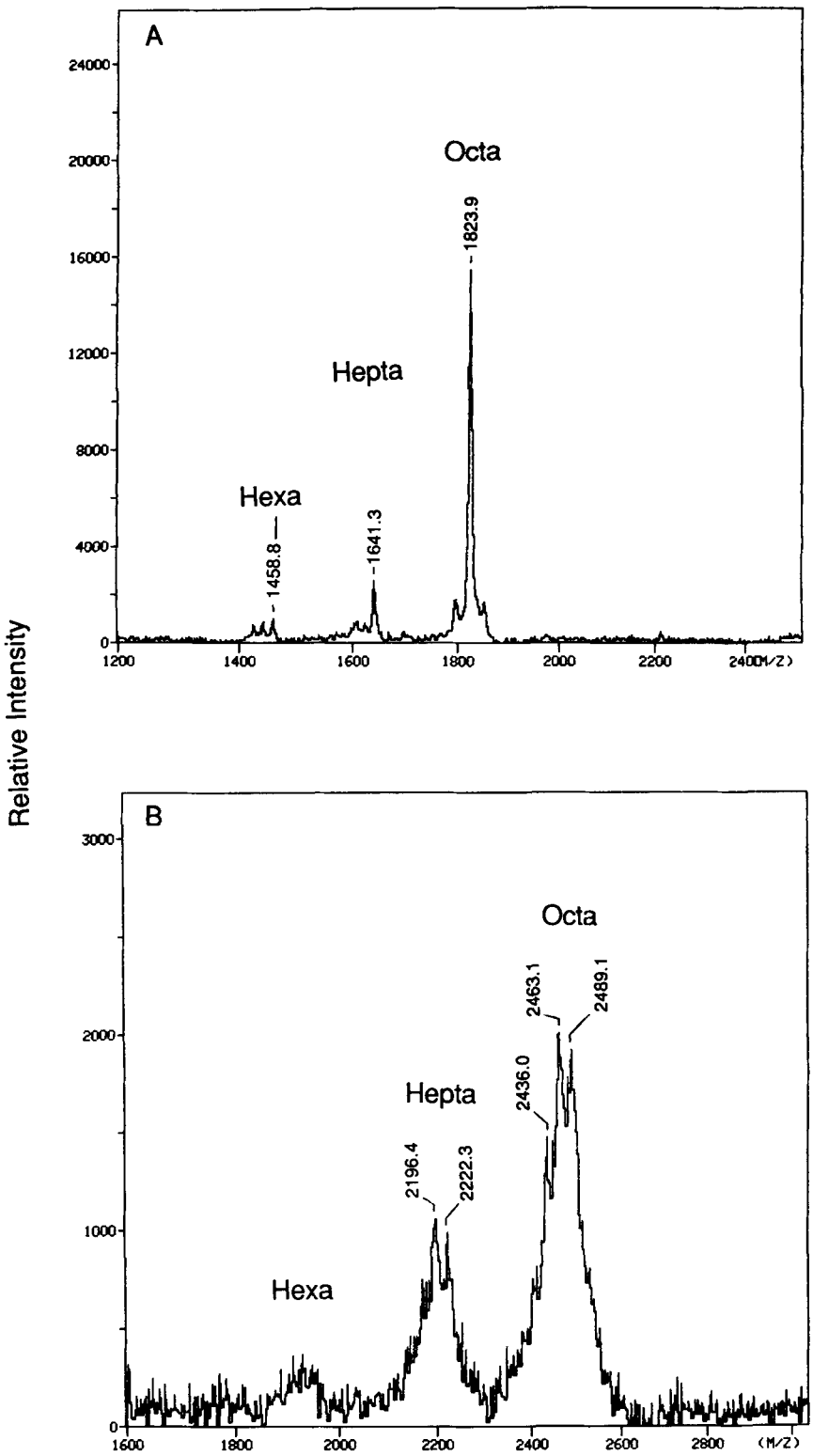


FIG. 5. Plasma desorption mass spectra of (A) sucrose polylaurate and (B) an olestra mixture prepared from soybean oil fatty acids.

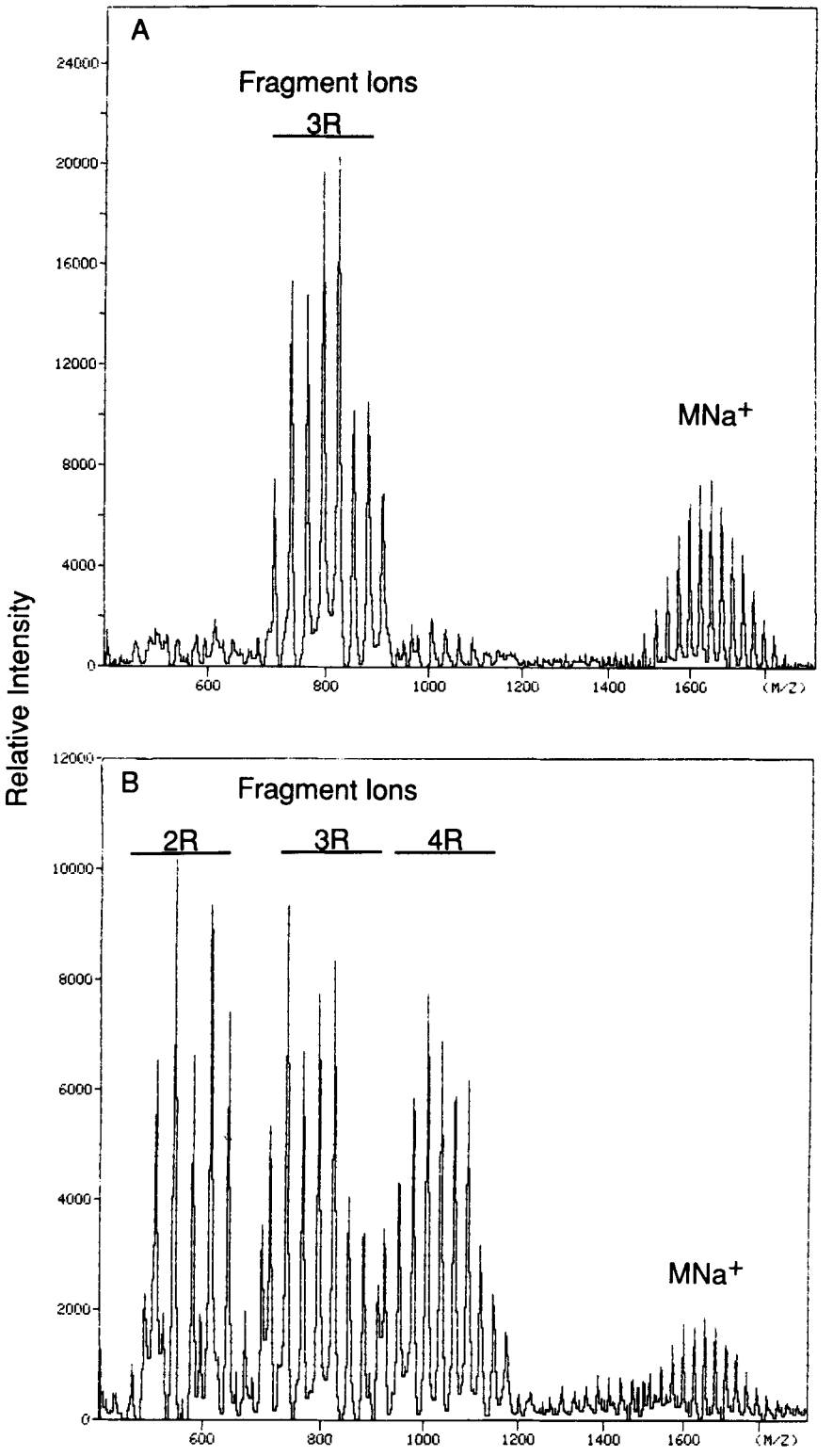


FIG. 6. Plasma desorption mass spectra of (A) a symmetrical hexaester and (B) a mixture of symmetrical and unsymmetrical hexaesters isolated from an olestra mixture synthesized with C_{12}–C_{18} fatty acids.

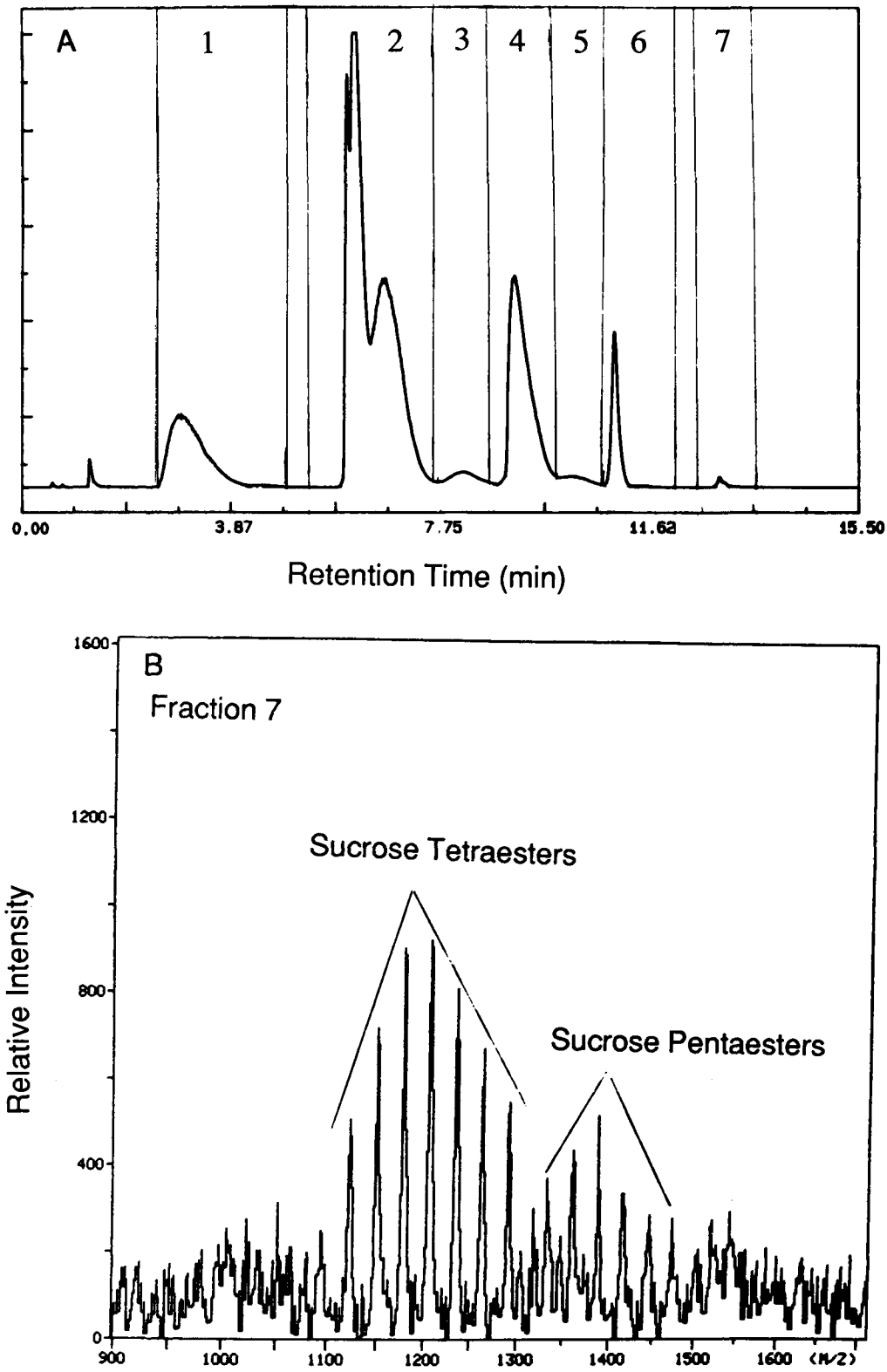


FIG. 7. (A) Reverse-phase HPLC chromatogram of an olestra mixture prepared with C_{12}–C_{18} fatty acids and (B) plasma desorption mass spectrum of HPLC fraction 7.

710, for the ion containing three laurate esters, to 962 for the ion containing three stearate esters. The trimodal distribution of fragments, evident in Figure 6B in the *m/z* 500–700, 700–900 and 900–1200 regions, indicates a mixture of hexaesters, some symmetrical, having three R's on each of the rings, and some unsymmetrical, having either 2 or 4 R's on each ring. The range of *m/z* values expected for the fragment ions containing only two fatty acid groups is from 528 to 696, while the mass range expected for the fragment ions containing four substituents is from 892 to 1229.

Figure 7A displays a reverse-phase HPLC chromatogram of an olestra mixture produced from the C_{12}, C_{14}, C_{16} and C_{18} fatty acids. A total of 2 mg was injected and seven fractions, as indicated, were collected for PDMS characterization. Excellent-quality spectra were obtained on all of the fractions, including 3, 5 and 7, which are minor components. Fraction 7, for example, represents only 0.3% of the chromatographic area or about 6 μg of total mass. This fraction was diluted into 50 μL of hexane/benzene and a 10-μL aliquot of that solution was analyzed. This corresponds to analysis of about 1 μg of total mass. A spectrum having an excellent ratio of signal-to-noise, Figure 7B, demonstrating the presence of both tetra- and pentaesters, was obtained. Note that about 10 major components are evident in the spectrum. This suggests that spectra of acceptable quality can be obtained on less than 100 ng of single-chain HPLC isolates. Some of the more abundant fractions, such as 2 and 4, were diluted by factors of up to 100 prior to analysis.

All previous FABMS attempts to identify olestra dimer components, in olestra mixtures heated to frying temperatures, failed. No ions were formed in the expected molecular weight region. However, size-exclusion chromatography revealed components with retention times consistent with those expected for dimeric products (15). The PD mass spectrum obtained from an isolate of heated olestra, having a retention time consistent with that expected for an olestra dimer, is shown in Figure 8. The sample was prepared from soybean oil fatty acids. Its fatty acid

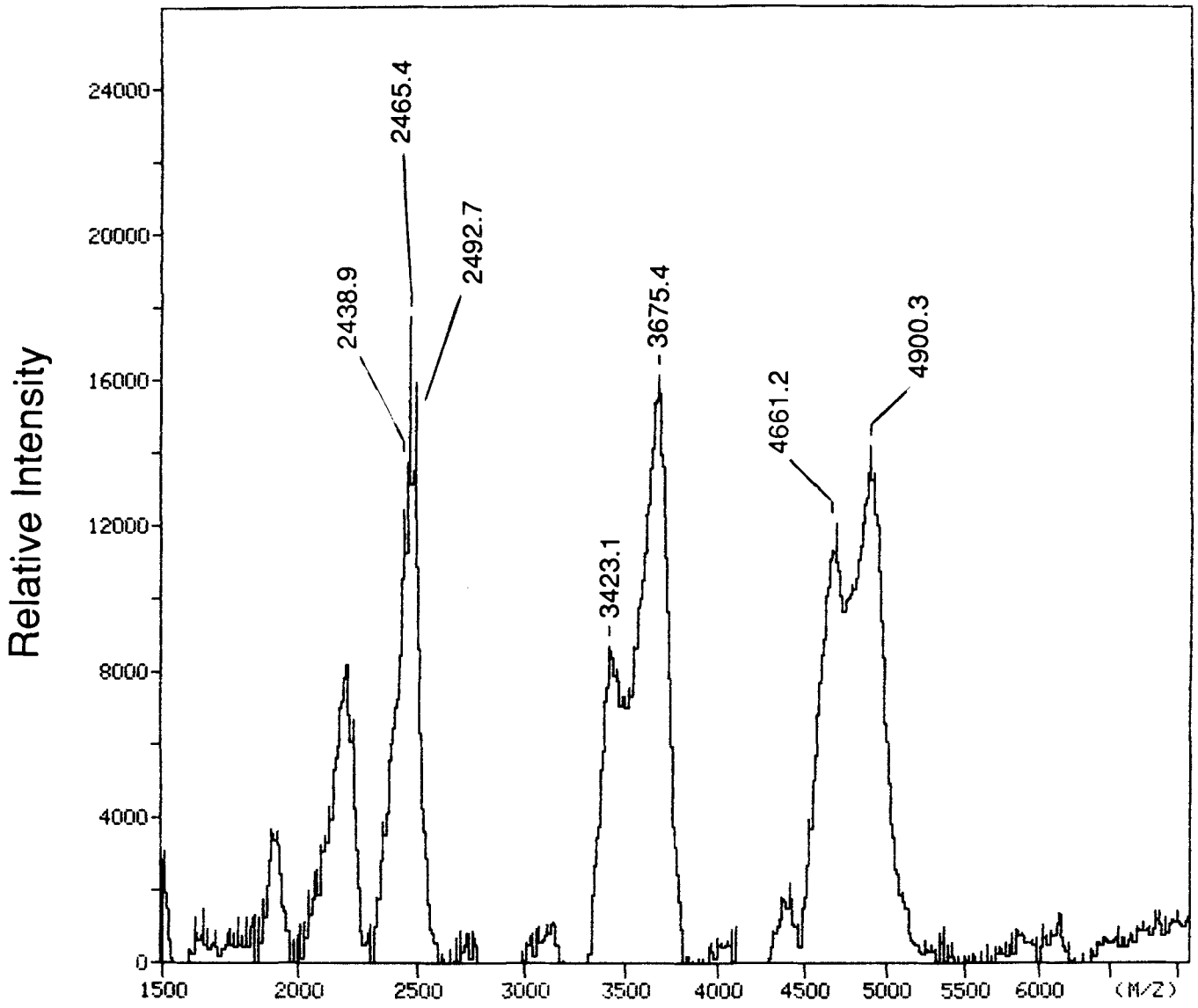


FIG. 8. Plasma desorption mass spectrum of the olestra dimer.

composition and the structure of the dimeric product are summarized elsewhere (15). The PD mass spectrum exhibits a broad, unresolved doublet of ions in the 4500–5000 dalton mass range. The peak centered at 4900 daltons corresponds to intact dimer formed from the condensation of two octaester monomers. The measured mass is close to that calculated (calculated $MNa^+ = 4907$ daltons) based on the average fatty acid composition of the monomer. The lower-mass peak in the doublet may contain contributions from the MNa^+ ion formed between octa- and heptaester monomers (calculated mass = 4644 daltons); however, the measured mass is somewhat higher than calculated, suggesting another unidentified contributor(s) to this signal. Higher mass resolution would obviously be helpful in this situation. The ions in the 3400–3700 dalton range have masses approximately equal to those calculated for fragment ions formed by glycosidic bond cleavage. Glycosidic cleavage of the protonated dimer would produce an ion having a calculated average mass of 3672 daltons. Finally, the ions in the 2000–2500 dalton range are MNa^+ ions from unresolved monomer also contained in the fraction.

All three of the desorption ionization techniques described here can be used to determine olestra molecular weights. FAB and PD are applicable to the sample levels normally isolated by HPLC. FAB is most appropriate for applications requiring higher resolution or more accurate mass assignment than can be achieved with PDMS. On the other hand, PD is the most convenient technique, especially for wide-mass-scan applications, and it is the tool that we use for initial low-resolution screening of unknown olestra components. PDMS is the only desorption ionization method, of the three investigated, that allows observation of the dimeric species produced during heating of olestra.

ACKNOWLEDGMENTS

We thank H.R. Morris (Imperial College, London) and D. Hazelby (Kratos Ltd., Ramsey, NJ) for obtaining field desorption spectra of sucrose octaoleate and sucrose octapalmitate.

REFERENCES

1. Matson, F., and R. Volpenhein, *J. Lipid Res. 13*:325 (1972).
2. Matson, F., and G. Nolen, *J. Nutr. 102*:1171 (1972).
3. Odam, G., and E. Stenhagen, in *Biochemical Applications of Mass Spectrometry*, edited by G.R. Waller, John Wiley and Sons, New York, NY, 1972, pp. 229–249.
4. Wood, G.W., in *Biochemical Applications of Mass Spectrometry*, edited by G.R. Waller, and O.C. Dermer, John Wiley and Sons, New York, NY, 1980, pp. 173–209.
5. Beynon, J.H., *Mass Spectrometry and Its Application to Organic Chemistry*, Elsevier, Amsterdam, Netherlands, 1960.
6. Harrison, A.G., *Chemical Ionization Mass Spectrometry*, CRC Press, Boca Raton, FL, 1983.
7. Barber, M., T.O. Merrin and W. Kelly, *Tetrahedron Lett. 18*:1063 (1964).
8. Keough, T., and A.J. DeStefano, *Org. Mass Spectrom. 16*:527 (1981).
9. Murata, T., and S. Takahashi, *Anal. Chem. 49*:728 (1977).
10. Pachuta, S.J., and R.G. Cooks, *Chem. Rev. 87*:647 (1987).
11. K.L. Busch, in *Methods of Surface Characterization*, edited by A.W. Czanderna, and D.M. Hercules, Plenum Surface Analysis Series, Vol. 3, in press.
12. *Soft Ionization Biological Mass Spectrometry*, edited by H.R. Morris, Heyden, London, England, 1980.
13. *Desorption Mass Spectrometry*, edited by P.A. Lyon, American Chemical Society Symposium Series no. 291; American Chemical Society, Washington, DC, 1985.
14. Sanders, R.A., A.J. DeStefano, R.S. Ampulski and K.R. Compson, Paper Presented at the 25th Annual Conference on Mass Spectrometry and Allied Topics, Washington, DC, May 29–June 3, 1977, pp. 57–58.
15. Gardner, D.R., and R.A. Sanders, *J. Am. Oil Chem. Soc. 67*:788 (1990).
16. Beckey, H.D., *Principles of Field Ionization and Field Desorption Mass Spectrometry*, Pergamon, Oxford, England, 1977.
17. Wood, G.W., *Mass Spectrom. Rev. 1*:63 (1982).
18. Beckey, H.D., E. Hilt and H.R. Schulten, *J. Phys. E: Sci. Instr. 6*:1043 (1973).
19. Beckey, H.D., *Int. J. Mass Spectrom. Ion Phys. 2*:500 (1969).
20. Kummler, D., and H.R. Schulten, *Org. Mass Spectrom. 10*:813 (1975).
21. Barber, M., R.S. Bordoli, R.D. Sedgwick and A.N. Tyler, *J. Chem. Soc. Chem. Commun.*:325 (1981).
22. Keough, T., *Anal. Chem. 57*:2027 (1985).
23. Glower, J.L., *Biomed. Mass Spectrom. 12*:191 (1985).
24. DePauw, E., *Mass Spectrom. Rev. 5*:191 (1986).
25. Hakansson, P., I. Kamensky, B. Sundqvist, J. Fohlman, P. Peterson, C.J. Mc Neal and R.D. Macfarlane, *J. Am. Chem. Soc. 104*:2948 (1982).
26. Sundqvist, B., and R.D. Macfarlane, *Mass Spectrom. Rev. 4*:421 (1985).
27. Jonsson, G.P., A.B. Hedin, P.L. Hakansson, B.U.R. Sundqvist, B.G.S. Save, P.F. Nielsen, P. Roepstorff, E.K. Johansson, I. Kamensky and M.S.L. Lindberg, *Anal. Chem. 58*:1084 (1986).
28. McNeal, C.J., R.D. Macfarlane and E.L. Thurston, *Ibid. 51*:2036 (1979).
29. Constantin, C., *Chemical and Chromatographic Studies on Dimeric Fatty Acids*, Dissertation, University of Illinois, 1986.
30. Paquette, G., D.B. Kupranycz and F.R. van de Voort, *Can. Inst. Food Sci. Technol. J. 18*:197 (1985).
31. Nawar, W.W., *Food Chemistry*, Dekker, New York, NY, 1985, pp. 139–244.
32. Figge, K., *Chem. Phys. Lipids 6*:159 (1971).
33. Arrendale, R.F., R.F. Severson, V.A. Sisson, C.E. Costello, J.A. Leary, D.S. Himmelsbach and H. van Halbeek, *J. Agric. Food Chem. 38*:75 (1990).

[Received November 25, 1991; accepted April 7, 1992]