SpiralTOF™

MALDI-Imaging MS of Lipids on Mouse Brain Tissue Sections Using Negative Ion Mode

Introduction

The main biological functions of lipids include energy storage, signaling, and acting as structural components of cell membranes. Not only their chemical composition and structures but also the distributions in biological body are important for biochemistry. Matrix-assisted laser desorption/ionization imaging mass spectrometry (MALDI-Imaging MS) is a powerful tool for the biochemical analyses of surfaces. Different lipid types are observed in positive or negative-ion MALDI mass spectra, depending on the presence of polar functional groups. Phosphatidyl cholines and galactosyl ceramides were mainly observed in the MALDI-Imaging MS of positive ion mode using JMS-S3000 SpiralTOF[1].

In this work, we report the use of the SpiralTOF for negative-ion MALDI-Imaging MS of sulfatides. High-resolution, accurate mass data and MS/MS data obtained under high-energy CID conditions provide information about structures, elemental compositions, and localization of many types of sulfatides.

Experimental

A mouse brain tissue section was placed on an ITO conductive glass slide plate (Fig. 1). The matrix compound 9-aminoacridine was sprayed on the surface of the tissue and then the sample was introduced to the mass spectrometer. The imaging MS measurements were performed in negative-ion mode on the whole brain tissue section (6.3 mm × 9.24 mm) with 60 µm spatial resolution. The images consisted of 16170 mass spectra equivalent to the accumulation of 500 laser shots for each mass spectrum.

Results and Discussion

The averaged mass spectrum of all pixels is shown in Fig. 2. The base peak ion at nominal *m/z* 888.6 was assigned as sulfa-

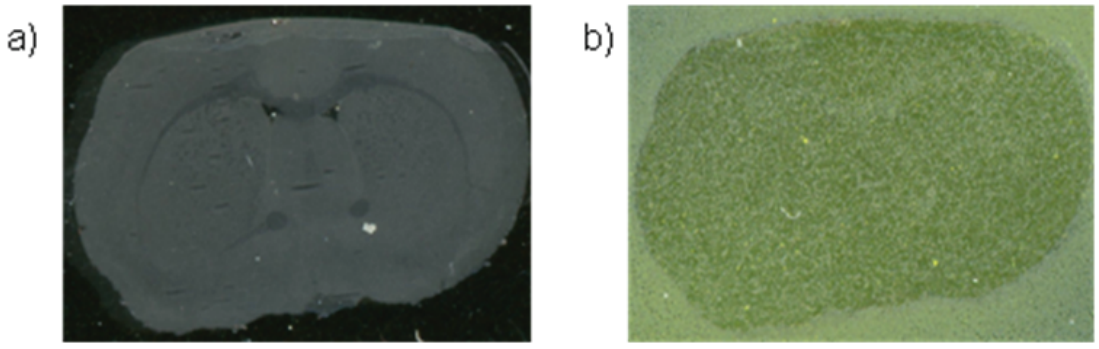

Figure 1. A mouse brain tissue on an ITO coated glass plate.
a) before matrix coating, b) after matrix coating

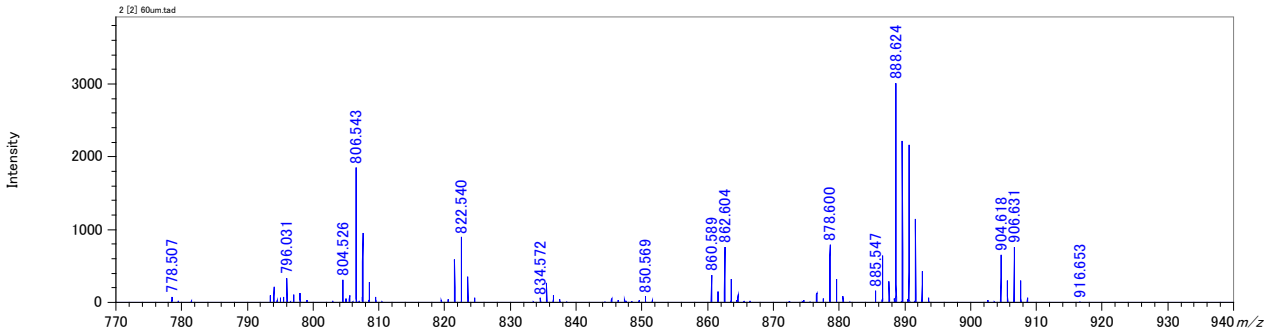

Figure 2. Averaged mass spectrum of mouse brain tissue.

MS-060413A

tide C24:1[M-H]$^-$. Structural analysis using TOF-TOF mode confirmed the assignment. The product-ion mass spectrum for *m/z* 888.6 is shown in Fig. 3. The structural formula and expected fragmentation channels of sulfatide C24:1 [M-H]$^-$ are also shown in Fig. 4. The observed peaks in Fig. 3 are a very good match with the expected fragmentation channels shown in Fig. 4. The clear observation of charge-remote fragmentation in *m/z* > 600 due to high-energy collision induced dissociation is a characteristic feature of the SpiralTOF, which provides high-quality structural information for lipids.

For the accurate mass analysis, the averaged spectrum was mass corrected by a single point calibration using the calculated *m/z* 888.6240 of confirmed sulfatide C24:1 [M-H]$^-$. The results of composition estimation of major peaks observed in the averaged mass spectrum are shown in Table. 1. Nearly all compounds were assigned within 5 ppm mass error. The mass images of all compounds listed in Table.1 are shown in Fig. 5. The phosphatidylinositol (PI) (38:4) (Fig.5 Image #8) is uniformly distributed on mouse brain tissue section. On the other hand, all sulfatides are localized in the same characteristic region. Because the different types of lipids are observed by MALDI-Imaging measurement both in positive[1] and negative ion mode, measurements made using both polarities provide complementary information about the nature and distribution of lipids in tissue sections.

Acknowledgment

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Reference

[1] Takaya Satoh et al., ***Mass Spectrometry***, Vol. 1 (2012), A0013

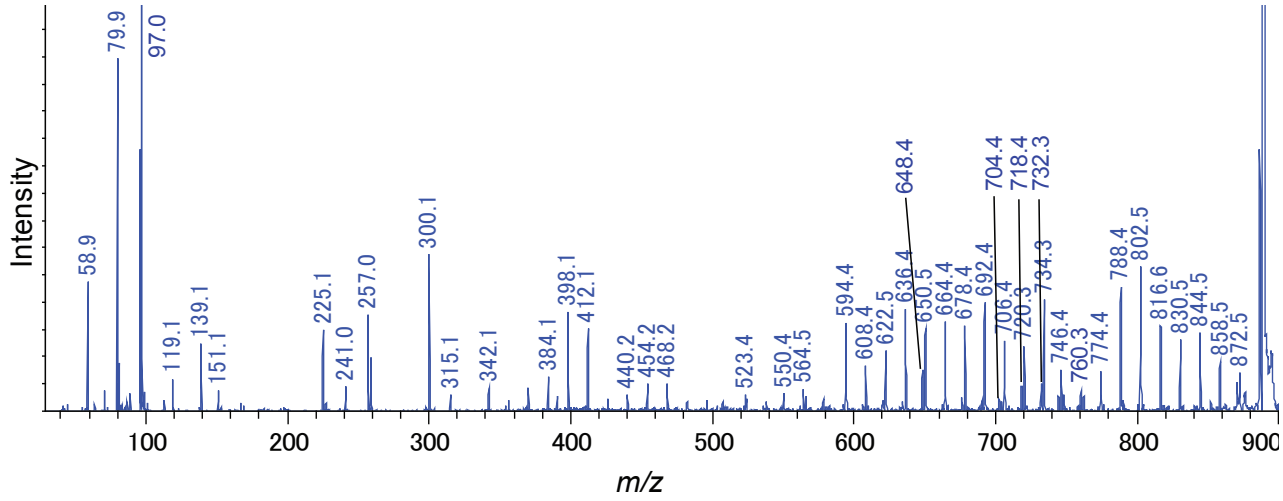

Figure 3. Product-ion mass spectrum of the ions corresponding to the peak at *m/z* 888.6.

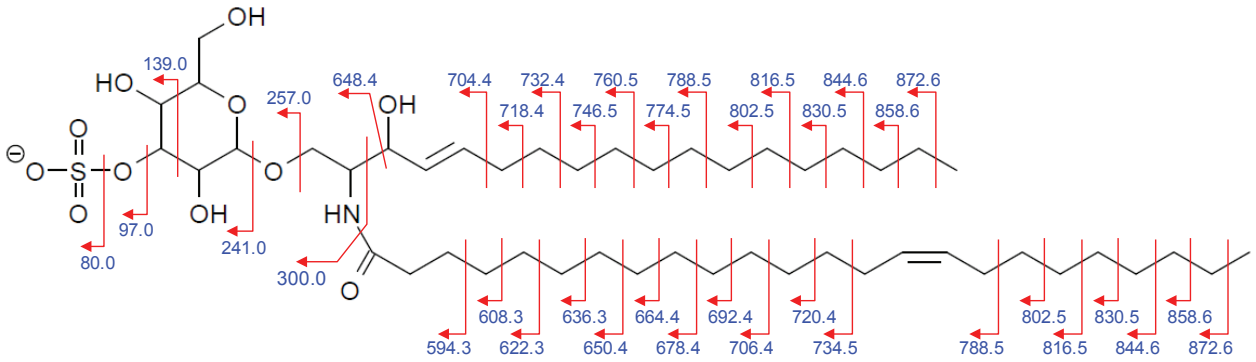

Figure 4. Structure and peak assignments of Sulfatide C24:1.

Number	Compound	Formula	*m/z* value (Observed)	*m/z* value (Calculated)	Error [mu]	Error [ppm]
1	C16 Sulfatide	$C_{40}H_{76}NO_{11}S$	778.5070	778.5145	-7.5	-9.6
2	C18 Sulfatide	$C_{42}H_{80}NO_{11}S$	806.5426	806.5458	-3.2	-3.9
3	C18-OH Sulfatide	$C_{42}H_{80}NO_{12}S$	822.5398	822.5407	-0.9	-1.1
4	C20 Sulfatide	$C_{44}H_{84}NO_{11}S$	834.5718	834.5771	-5.3	-6.3
5	C20-OH Sulfatide	$C_{44}H_{84}NO_{12}S$	850.5694	850.5720	-2.6	-3.0
6	C22 Sulfatide	$C_{46}H_{88}NO_{11}S$	862.6037	862.6084	-4.7	-5.4
7	C22-OH Sulfatide	$C_{46}H_{88}NO_{12}S$	878.6003	878.6033	-3.0	-3.4
8	PI(38:4)	$C_{47}H_{82}O_{13}P$	885.5466	885.5499	-3.2	-3.7
9	C24:1 Sulfatide	$C_{48}H_{90}NO_{11}S$	888.6240	888.6240	—	—
10	C24:1-OH Sulfatide	$C_{48}H_{90}NO_{12}S$	904.6179	904.6189	-1.0	-1.1
11	C24-OH Sulfatide	$C_{48}H_{92}NO_{12}S$	906.6308	906.6346	-3.8	-4.2
12	C26:1 Sufatide	$C_{50}H_{94}NO_{11}S$	916.6529	916.6553	-2.4	-2.6

Table 1. Differences between calculated and observed m/z values for peaks observed in the averaged mass spectra after mass-correction using confirmed Sulfatide C24:1.

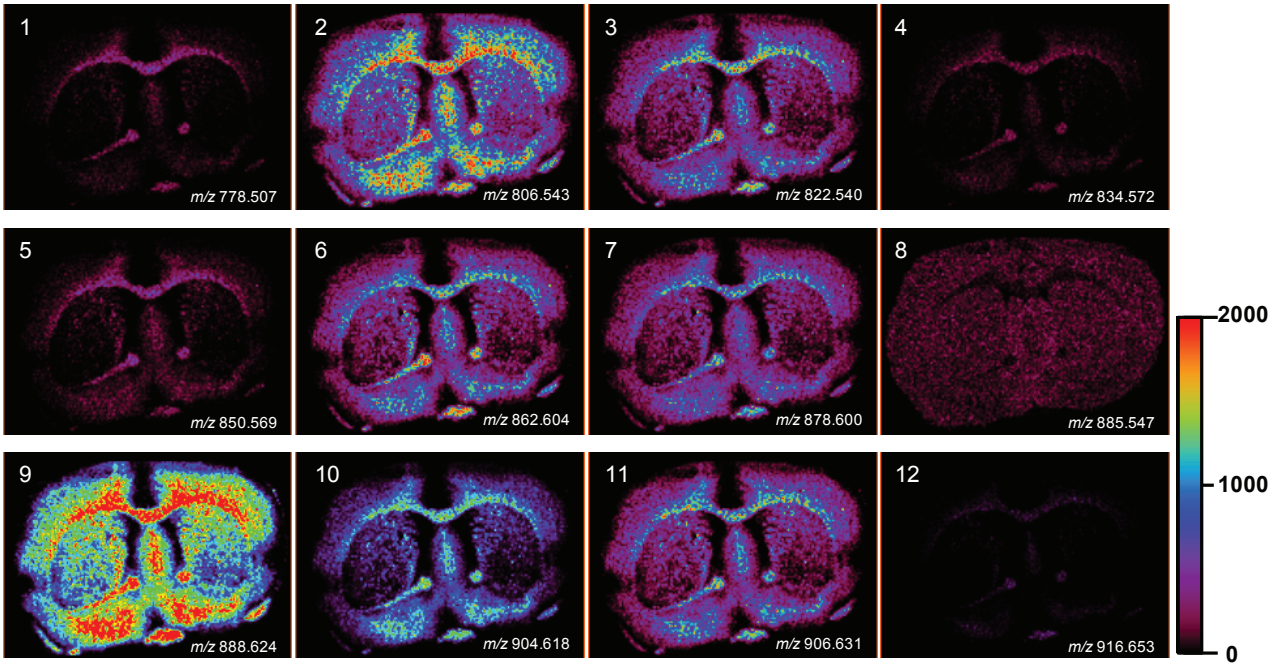

Figure 5. Mass images of compounds from mouse brain tissue.