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Structural Investigation of N-lignoceroyl (C24:0) sphingomyelin bilayers

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Introduction

Sphingomyelin (SM) is one of major sphingolipid components for many animal cell plasma membranes. Recently, it has been reported that SM is involved in various essential biological phenomena. The interaction between SM and cholesterol is believed to be a key factor for the formation of so-called "lipid rafts"

Naturally occurring SMs are chemically heterogeneous and contain molecular species of asymmetric chain length, i.e., the length of the amide-linked acyl chain is frequently longer (22 or 24 carbons) than that of the sphingosine chain of mostly 18 carbons. Such high asymmetric lipid species are very seldom found in naturally occurring glycerophospholipids, especially for phosphatidylcholine species of animal tissues.

The structure and phase behavior of the most typical asymmetric SM, N-Lignoceroyl (C24:0) SM, have been investigated by means of various physical methods. For the hydrocarbon chain packing mode, a structural model proposed based upon spectroscopic data [1] disagrees with that proposed based upon X-ray diffraction (XRD) data [2,3]. Using SR-XRD, we re-examined the structures of hydrated C24:0 SM bilayers, paying attention to the hydrocarbon chain packing mode [4].

Materials and methods

C24:0 SM was produced by semi-synthesis from naturally occurring bovine brain sphingomyelin (BSM), using the deacylation-reacylation method.

Static X-ray diffraction (XRD) measurements were carried out at the beamline 15A of PF, using a short camera length setting to observe until higher order lamellar reflections. The sample-to-detector distance was ~280 mm and imaging plate (IP) was used as the detector. Temperature-scan simultaneous small angle x-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) measurements were performed at the beamline 9C of PF, with a wavelength of 0.150 nm.

Results and discussion

Temperature-scan SAXS-WAXD measurements were carried out to clarify structural change sequence associated with phase transitions. As a result, we found that C24:0 SM bilayers form a ripple phase just below the chain melting transition (Fig.1). It has been speculated the possibility of a ripple phase formation from analogy with BSM bilayers. Our result is a first experimental confirmation.

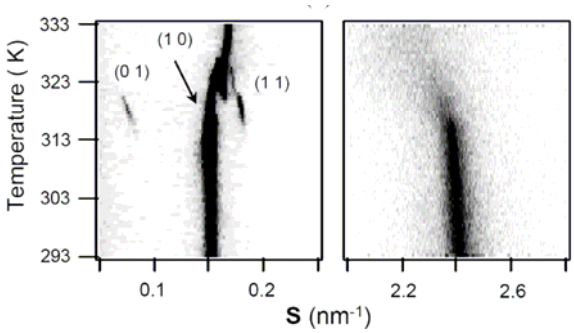

Fig. 1 Gray-level plot of SAXS/WAXD intensities as a function of temperature for C24:0 SM bilayers during a heating scan at a rate of 2 K/min.

In order to investigate the hydrocarbon chain packing mode of C24:0 SM bilayers, we reconstructed electron density profiles from XRD data. The electron density profiles indicates that the hydrocarbon chains of C24:0 SM bilayers are packed into a partially interdigitated structure in both low- and high-temperature phases. Hence, it is likely that the partially interdigitated structure is also formed in the ripple phase that appears at the intermediate temperature region (Fig.2).

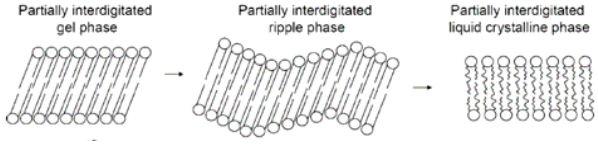

Fig. 2 Schematic representation of structural change of C24:0 SM bilayers in heating scan.

References

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