PE3.02 Raman spectroscopic differences between lard and tallow 48.00

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***Abstract*— Using Raman spectroscopy, crystals of meat fats were investigated especially for their polymorphisms. We also assessed the feasibility of Raman microscope for this study. Lard and beef tallow samples were prepared by rendering down porcine and bovine *subcutaneous* adipose tissues. The melts of these fats were crystallized at the cooling rate of -0.1°C/min and kept at 5°C during Raman measurements. Raman spectra of the crystals were acquired using a confocal Raman microscope with 785-nm-laser excitation. As the result, the differences were observed in Raman spectra of the crystals, although they were likewise composed of TAG (triacylglycerol) molecules. Lard had a distinctive band at 1416 cm^{-1} in the region of C-H bending mode, which is derived from the orthorhombic subcell structure of *β'* crystal form. The present results let us to conclude that Raman microscopy is able to provide the significant information of polymorphs of TAG systems such as lard and beef tallow.**

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***Index Terms*— triacylglycerol, crystal, polymorphism, Raman microscopy.**

I. INTRODUCTION

Triacylglycerols (TAGs) form a large group of lipids, and they are the main constituents of lard and beef tallow. TAGs consist of a glycerol backbone and three esterified fatty acids. There are many TAG molecules, according to their fatty acid composition and the positional distribution of these fatty acids on the glycerol backbone.

One of the important features of TAGs is polymorphism. Polymorphism is defined as the existence of several crystalline phases with the same chemical composition that have a different structure [3]. In the case of TAGs, three main polymorphic phases, *α*, *β'*and *β*, according to their hydrocarbon subcell packing, have been determined [5, 6]. Polymorphism of TAG influences on fat physical properties, and different polymorph gives different functional characteristics for the fat: plasticity, britness, lubricity etc.

Polymorphism of TAGs has been investigated using synchrotron radiation X-ray beams, differential scanning calorimetry, FT-IR and Raman-scattering measurement. Regarding to the heterogeneous systems composed from variety of TAG molecules such as lard and beef tallow, it is difficult to investigate their polymorphisms. In this study, we try to acquire the information of polymorphs of these meat fats using Raman microscope, and assess the feasibility of Raman microscope for the study on fat polymorphisms.

II. MATERIALS AND METHODS

a. Samples

Lard and beef tallow samples were prepared by rendering down porcine and bovine *subcutaneous* adipose tissues: Liquid-nitrogen-frozen tissues were finely ground by pestles, and dry rendered at 75°C for 15 min. Immediately after the rendering, hot samples were refined by means of centrifugation. Refined samples were stored at -30°C for further studies.

b. Crystal formation

Samples were melted at 80°C for 15 min in order to destroy any crystal memory. 10 μl of melts were placed in a quartz bottom dish whose temperature was held at 40°C. After keeping 40°C for 30 min, melts were crystallized at the cooling rate of -0.1°C/min. Samples were kept at 5°C during Raman measurements.

c. Raman measurements

785-nm-laser excited Raman spectra of lard and tallow were acquired using Raman microscope. Samples were placed in a temperature-controlled quartz bottom dish. The back-scattered Raman light from the sample was collected by an objective lends and detected with a near-infrared multichannel detector. The laser power at the sample was 100 mW, and the accumulation time was 20 sec. Laser beam was about 1 μm in diameter.

III. RESULTS AND DISCUSSION

Although visually-different types of crystal were observed on the process of cooling, it seemed only one polymorph was observed at 5°C in each fat

(Fig. 1). Lard showed a granular morphology composed of a large number of small crystals. On the other hand, beef tallow forms a conspicuous polycrystal made up of needle crystals.

Raman spectra of the crystals of lard and beef tallow are shown in Fig. 2. We can tell that they are the spectra of 'crystal' partly due to the existence of the band at 1171 cm^{-1}, concerning CH_2 rocking mode [7]. These two spectra were different each other especially in the spectral range 1140–1040, 1430–1410 and 1770–1720 cm^{-1}, although these crystals were likewise composed of TAG molecules.

In the region of C-H bending mode, lard crystal had a distinctive band at 1416 cm^{-1}, which is derived from the orthorhombic subcell structure of β' crystal form [8]. It is known, however, that lard tends to be crystallized in the β form [3, 4]. It might be because of the relatively rapid cooling rate which induces metastable crystal form, β' [2].

The 1770–1720 cm^{-1}-spectral range concerning C=O stretching mode also reflects polymorphic phases of TAGs [1, 9]. As these previous studies indicate, both spectra were composed of more than two bands in this range (data not shown). This is due to the existence of more than two geometries of ester C=O. We are conducting the analysis of C–H-stretching-spectral region for further understanding of polymorphs of lard and tallow.

The polymorphs differ in stability, melting point, melting enthalpy, and density [3]. Therefore, it is easy to expect polymorphism could be the key to understand meat fat qualities such as 'firmness' and 'luster', which have been little explained. From the present results, we can say that the Raman microspectroscopy, which can provide us the significant information of polymorphism of meat fats, has the great potential to unveil meat-fat quality.

IV. CONCLUSION

The Raman spectra of the crystals of lard and beef tallow were different each other at 5°C. They were especially different in the spectral range 1140-1040, 1430-1410 and 1770-1720 cm^{-1}. They were mainly because of the difference in crystal forms (polymorphs). The present results let us to conclude that Raman microscopy is able to provide the significant information of polymorphs of heterogeneous TAG systems such as lard and beef tallow.

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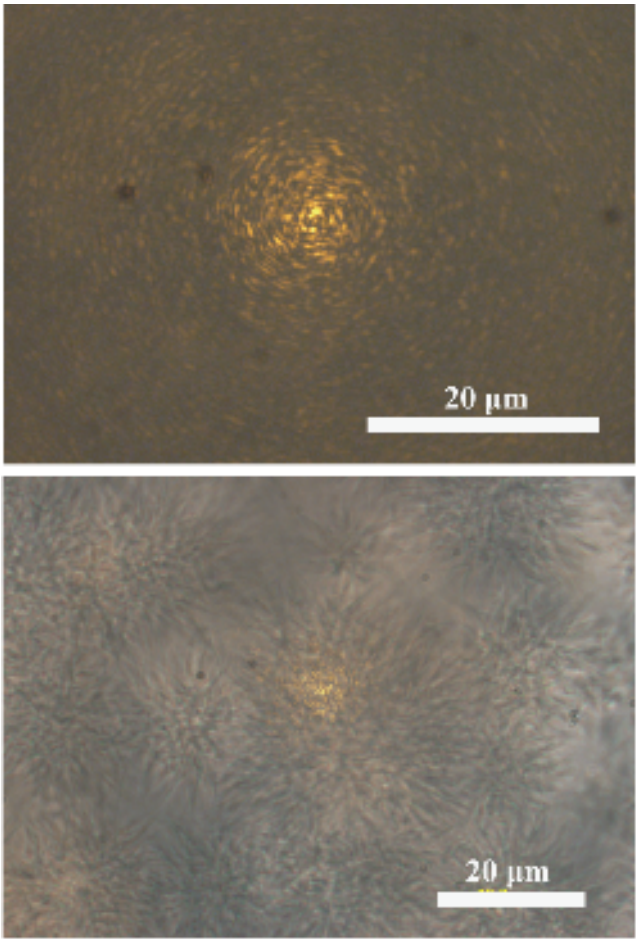

Fig.1 Morphology of lard and beef tallow at 5°C. Lard contained a lot of indistinct-shaped small crystals. Beef tallow showed needle crystals forming polycrystals. The bright area at the center were the scattering of laser beam.

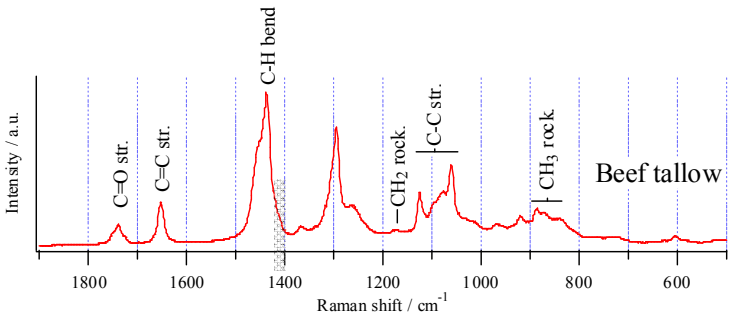

Fig. 2 An example of Raman spectrum of animal fats at 5°C. A band will arise at 1416 cm^{-1}, shaded in the figure, when crystals have the orthorhombic subcell.