

MERIT Internship Report

August 25th, 2022.

Department of Chemistry, Graduate School of Science

2nd grade Master Course • 11th term MERIT-WINGS

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※ This report is partially abstracted in order to protect unpublished data.

■ Host Organization

Department of Applied Chemistry, School of Engineering, The University of Tokyo
Prof. Fujita Laboratory

■ Period

July 20th, 2022 – August 19th, 2022

■ Research Topic

Mastering the Crystalline Sponge Method and its Application to Natural Product Chemistry

■ Background

I study natural product chemistry, and my daily research is broadly divided into the synthesis and structure determination of new molecules. Analytical tools are used in structure determination, such as mass spectrometry, nuclear magnetic resonance (NMR), infrared, visible, and ultraviolet spectroscopy, and single-crystal X-ray structure analysis. Among these analytical methods, single-crystal X-ray structure analysis is a very powerful tool that shows the three-dimensional structure of a molecule with the highest reliability. However, single-crystal X-ray structure analysis requires crystallization of the target compound, which has often been avoided because of the difficulty of crystallization. Therefore, I focused on the "Crystalline Sponge Method", which does not require the crystallization process. In this method, a single-crystal sample for measurement can be prepared simply by soaking a porous crystal called a crystalline sponge in a solution of the target compound, so the crystallinity of the target compound does not matter at all, and a single-crystal sample can be obtained even from an oily sample. In addition, since the sample can be prepared from a single crystal grain of 100 μm square, it is possible to analyze even nanogram quantities of the sample. In other words, the crystalline sponge method is a very useful technique for natural product chemistry research to determine

the structure of oily samples and trace samples, and rapid progress in research will be expected when I mastered this method. Therefore, I decided to do a MERIT internship in the Fujita Laboratory, where the crystal sponge method was developed.

■ Activity Overview

In this internship, we learned the crystalline sponge method at the Mitsui Link-Lab in Kashiwanoha, and reproduced and utilized the techniques at the Hongo Campus. The following is a summary of the series of experimental operations of the crystalline sponge method that were acquired through this internship.

① Preparation of Crystalline Sponge

The crystalline sponge was prepared according to a previously published method (*Nature* **2013**, *495*, 461-466.). A nitrobenzene solution of tris(4-pyridyl)triazine was prepared in the lower layer of a test tube with a lid, and a methanol solution of zinc iodide in the upper layer. The crystals were allowed to stand in the two-layer system for about 3 days. The solvent that filled the crystals was then replaced with n-hexane over the next 5 days.

② Inclusion of Compound

Crystals showing good polarization were selected under a microscope and transferred one grain at a time into a microvial. A solution of the guest compound was added to the vial, and the solvent was volatilized through a pinhole in the lid of the vial over a period of two days.

③ X-ray Structural Analysis

Structural information was obtained by applying laboratory-scale X-ray and analyzing the diffraction points.

In the end, I was able to complete all processes from ① Preparation of Crystalline Sponge to ③ X-ray Structural Analysis in the Chemistry West Building at the Hongo Campus. In the future, I would like to apply this technique to further develop natural product chemistry.

■ Acknowledgment

I would like to express my deepest gratitude to Project Professor Sota Sato for his willingness to accept this internship plan and for his kind instructions. I would also like to express my sincere gratitude to Mr. Satoshi Yoshida for his careful guidance on experimental operations and analysis methods. Finally, I would like to express my sincere gratitude to the MERIT-WINGS program for supporting this internship program.