Chika Kuroda:

Research on the Constitution of Natural Coloring Matters and Her Life as a Pioneering Woman Chemist

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She was born in Saga in 1884 as a daughter of a samurai family. At the beginning of the Meiji era (from 1867), Japan drastically changed from a feudal nation to a modern one.

Her father, Heihachi Kuroda, recognized that education would become important in the future and it was necessary to provide a high level of education for his children including his girls. Attendance from age 14 for three years at Saga shihan joshi-bu (normal school for women) was a decisive step in Chika's career. After one year of teaching duty at an elementary school, she moved to Tokyo for entrance into Jokohshi (higher normal school for women). For the entrance examination, she chose the scientific department rather than that of culture. The lectures on general chemistry and the guidance on experimental training in chemistry were given by Toshio Hirata, who was the only professor in the chemistry department. Kuroda was interested in chemistry, especially organic chemistry, and wanted to study much more, but in Japan, universities were closed to females.

After graduating from Jokohshi, she got a job as a teacher at Fukui shihan joshi-bu. When she was 23 years old, she was recommended to attend the special training course for teachers of Jokohshi, so she returned to Tokyo. This was the first case in the chemistry department. For the two-year training, she studied by herself on inorganic, organic, analytical and theoretical chemistry and also differential, integral calculus, etc. using English textbooks. When she finished this course, she was appointed as an associate professor of Jokohshi. Around this time she met Nagayoshi Nagai who was a part-time lecturer in the chemistry department and she used his guidance for preparation of an experimental demonstration during his lecture. In 1913, Tohoku Imperial University, which was newly founded in 1911 in Sendai, was the first to open its doors to both men and women. Nagai recommended that Kuroda should apply for the entrance examination in the chemistry department, and he also advised the president of Jokohshi to recommend her for application. In June 1913, she took the entrance examination along with more than 40 persons, and 13 persons including Kuroda and another girl (Mume Tange) passed the examination. For this reason a written protest was sent from the Ministry of Education to the chancellor of Tohoku Univ., because a female student has never been accepted by the Imperial University. The academic year opened in September, and Kuroda's new life as a student at the university started. In the chemistry department there were three professors ; Masataka Ogawa (Inorganic Chem.), Rikoh Majima (Organic Chem.) and Masao Katayama (Theoretical Chem.). When Kuroda had to decide which laboratory she would like to do her research for graduation, she chose the organic chemistry lab and told Majima of her interest in

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the constitution of natural coloring matter.

Majima immediately gave her the topic of Murasaki (Lithospermum Erythrohiom). At first Majima tried to get crystals of the coloring matter, because many chemists had tried crystallization, but nobody obtained the crystals. He succeeded in the crystallization within about one week. In her first experiment, the coloring matter was extracted with acetone from about 4 kg of roots from Murasaki using a Soxhlet extractor at about 40°C for a long time. The concentrated extract was treated using Majima's method, but the product obtained was tar with only a trace amount of crystals. She was surprised and understood that the coloring matter is very sensitive to heating. She then tried an extraction at room temperature without the Soxhlet extractor, and succeeded in obtaining crystals of the coloring matter of which she named Shikonin.

Experimental results on the structure determination were as follows : (1) Molecular formula is $C_{16}E_{16}O_5$, (2) Several coloring reactions showed that Shikonin is a phenolic compound, (3) Acetylation at 40°C gave a triacetyl derivative, (4) Ozonization of the triacetate gave 3, 6dihydroxyphthalic acid, succinic acid and acetone, (5) Zinc dust distillation of Shikonin gave naphthalene. Based on these results, she estimated the structure of Shikonin and submitted her first original paper to the Journal of Chemical Society of Tokyo in August 1918.

She then returned to Jokohshi as a professor. In November 1918 she orally presented the constitution of Shikonin in the meeting of the Chemical Society of Tokyo. This was the first case of a presentation of a chemical study by a woman chemist in Japan.

In spring of 1921 she visited England at the expense of the Japanese Government to study chemistry under the guidance of W. H. Perkin Jr. at Oxford Univ. and returned to Japan in August 1923. On September lst, 1923, the Tokyo area suffered from a disaster due to a big earthquake, and the buildings of Jokohshi were destroyed and/or burned by fire. Kuroda studied a new subject since early 1924 in a room of Majima's laboratory at the Institute of Physical and Chemical Research which was founded in 1921 at Komagome. Her work involved the constitution of Carthamin obtained from safflower. Many chemists in Europe and a Japanese chemist, Tokuhei Kametaka, had already studied in this field and Kametaka had obtained crystals of Carthamin, but the constitution was still not fully determined. Crystallization of Carthamin was very difficult as was that of Shikonin, and Kametaka's method using pyridine did not give pure crystals. She found a new method in which dry safflower was treated with diluted hydrochloric acid followed by crystallization using methanol to give yellow crystals. Recrystallization of the yellow crystals from pyridine gave red crystals. The red and yellow crystals were found to be isomeric compounds having the same molecular formula, $C_{21}H_{22}O_{11}$, and were named Carthamin and Isocarthamin, respectively. Catalytic hydrogenation and hydrolysis using diluted phosphoric acid showed that Carthamin exists as a glycoside. Based on the results of several coloring reactions and a precipitation reaction using lead acetate, and acetylation of aglycons from Carthamin, Carthamin was suggested to be hydroxychalcone. Finally, from a comparison of melting points of pentamethyl Carthamin with synthesized pentamethoxychalcone, she confirmed the structure of Carthamin, which was reported

in 1929. This work was her doctor thesis and she was awarded the Doctor of Science degree in 1929. This was the first case in the field of chemistry for Japanese women. Kametaka admired her for her passionate work and excellent techniques resulting in this achievement. From 1930 to 1936, she investigated the coloring matter of Awobana (commerina communis), Kuromame, Shiso and Nasu (eggplant) all of which are anthocyans. She obtained each aglycon as crystals and determined their structures, which were named Awobanin (awobana), Kuromamin (kuromame), Shisonin (shiso) and Nasunin (nasu).

After 1939, she studied the structure of pigments from spins of sea urchins (Aka, Murasaki, Bafun and Pipe). Each pigment obtained was a naphthoquinone derivrative, spinochrom, and the structure of SpAka was determined tin 1944. Recently, the structure was called spinochrom B. After World War I, Jokohshi changed to Ochanomizu Univ. and Kuroda became Prof. in the Faculty of Science at the university. In 1952, she retired from the university and was awarded an Emeritus professorship. Kuroda enjoyed doing research on the constitution of several natural coloring matters throughout her life for more than 50 years till she passed away in 1968.