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Application of derivatization pyrolysis gas chromatography/mass spectrometry to analysis of archaeological lacquerwares

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ABSTRACT

One piece from Mumujyana ruins and one piece from Urasoe Yōdore (a mausoleum), both belong to Ryukyu Kingdom, were analyzed by direct and derivative pyrolysis gas chromatograph/mass spectrometry (Py-GC/MS). Direct Py-GC/MS chromatogram at $m/z = 108$ of both samples showed that peaks of 3-pentadecylphenol and 3-heptadecylphenol were relatively weak, and the shape of peaks from low molecular weight component group formed a platform, different from the mountain type of the three standard *Toxicodendron vernicifluum, Toxicodendron succedanea*, and *Gluta usitata* lacquers. However, analysis of a mixture of the three kind lacquers and a sample of *T. succedanea* mixed with *T. vernicifluum* showed a similar platform shape on chromatogram at $m/z = 108$. In addition, in order to confirm this result, derivative Py-GC/MS was also performed, and the results are compared and discussed.

1. Introduction

Lacquer is one of the oldest natural coating materials and has been used for thousands of year due to its durability, water resistance, and chemical resistance. It is also used for protection and conservation of many important historical and cultural objects and arts and as an adhesive for combining objects [1–3].

There are three kinds of lacquer tree that produce lacquer sap in the world. *Toxicodendron vernicifluum*, which grows in China, Japan, and Korea, has urushiol (C15) the main lipid component, *Toxicodendron succedanea*, which grows in Vietnam and Taiwan, has laccol (C17) as the main lipid component, and *Gluta usitata*, which grows in Myanmar, Thailand, Lao, and Cambodia, has thitsiol (C17) as the main lipid component [4,5]. The geographic distribution and lipid structure are shown in Fig. 1 [6].

Lacquer sap self-polymerizes to form a film. It is a cross-linked polymer that polymerized by laccase and insoluble in many organic solvents. Only a few analytical techniques are available for the scientific investigation and identification of lacquer film, and Py-GC/MS analysis is one useful method for analyzing lacquer film because it requires no sample preparation or pretreatment and only a small amount of sample. In a Py-GC/MS chromatogram, the shapes of peaks differ due to the different structure of urushiol, laccol, and thitsiol; that is, these three lacquer species can be discriminated by the characteristics of their pyrolyzed products. However, because urushiol, laccol, and thitsiol have two hydroxyl groups with high polarity, they are easily adsorbed on column, which decrease the detection sensitivity. In order to solve this problem, derivatization reagents such as *N,O*-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) [7] and tetramethylammonium hydroxide pentahydrate (TMAH·$5H_2O$) [8–10] are usually used to increase detection sensitivity.

Differentiation of lacquer species help effectively in the study of archaeological materials. For example, it is useful in evaluating the archaeological value of lacquerware, choosing the same materials originally used in order to restore lacquer objects, and being able to understand ancient lacquer culture and trade scenarios. Ryukyu has a long history as an independent kingdom (AD1429–1879) and its trade with China, Southeast Asian countries, and Japan flourished. It is believed that Ryukyu lacquer manufacturing technology resulted from trade with the Chinese Ming dynasty, then, local characteristics were added, and gradually developed into a special Ryukyu lacquer culture.

Many lacquerware objects have been excavated from ruins of the Ryukyu Kingdom. We previously reported several analyses of Ryukyu lacquerwares by Py-GC/MS [11,12]. In general, comparisons of the Py-GC/MS chromatogram with the characteristic pyrolysis products identify the lacquer species of the archaeological remains unearthed from ruins. However, when two pieces of

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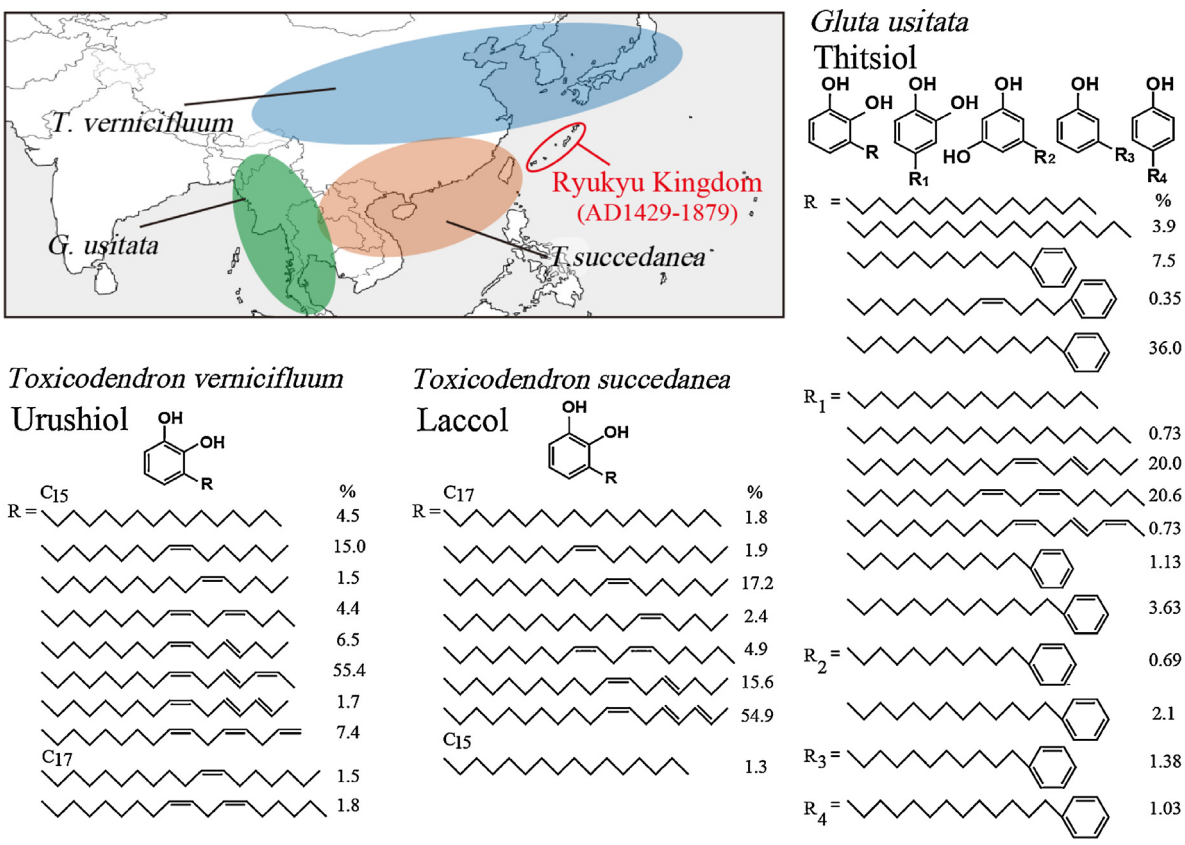

Fig. 1. Lacquer tree distribution and structure of urushiol, laccol, and thitsiol.

lacquer extracted from the lacquerware excavated from the ruins of Ryukyu Kingdom (AD1429–1879) were analyzed in this study, the ion chromatograms were not consistent with any of the three kinds of lacquer. It has reported that Ryukyu lacquerwares excavated from the Jōmon period are usually one of the three kinds of lacquer [13], it can be easily considered that long-term deterioration makes some samples inconsistent with the standard lacquer Py-GC/MS results. However, another reason, such as a mixture of lacquers also causes this phenomenon. In general, a lacquer object is usually coated with multiple layers, especially a precious lacquerware object. With the passage of time, lacquerware needs to be restored due to natural degradation, and the restoration process often uses the materials of the time. Therefore, probability of using mixed lacquers to produce and restore lacquer objects is very high. In order to verify this possibility and as part of a continuous research program, in this study, different ratios of standard samples were prepared and examined by Py-GC/MS. Then, the characteristics of pyrolysis products of the Ryukyu lacquerwares from the Mumujyana ruins and Urasoe Yōdore mausoleum were compared with pure and mixed standard lacquers, and the lacquer species, mixture percentage, and lacquer techniques of the period are discussed.

2. Experimental

2.1. Samples

A piece of lacquerware from the ruin of Mumujyana (sample A) and a piece from Urasoe Yōdore mausoleum (sample B), both found in Okinawa Prefecture, were used in this study. According to the Ryukyu history “Chuzanzeihu”, sample A is considered to date from 1500 years ago. The Urasoe Yōdore mausoleum is said to belong to King Eiso (reigned 1260–1299) and King Anne (reigned 1589–1620); that is, sample B is lacquerware of the 13th–15th century.

Standard lacquers collected from *T. vernicifluum* lacquer tree grown in China and a *G. usitata* grown in Myanmar were purchased from Minowa-Shikkou, Japan, and standard lacquer collected from *T. succedanea* lacquer tree grown in Vietnam was purchased from Dohi-Shoten, Japan. The percentages of each lacquer in mixed standard lacquers are summarized in Table 1.

The standard mixed lacquer film preparation was as follows: mixed lacquer saps were coated in a 70 × 70 cm glass plate at 76 μm wet thickness by an applicator and dried in a lacquer chamber at 25 °C and 70% relative humidity (RH) for 14 d. Then, they were removed from the chamber and stored in natural condition (room temperature and RH) in our laboratory for 18 months.

The derivatization reagents, *N*,*O*-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) (Sigma–Aldrich Co.) and tetramethylammonium hydroxide pentahydrate (TMAH·5H_2O) (Tokyo Kase Co., Ltd.) were used directly without further purification.

Table 1
Percentage of standard lacquers.

Entry	Sample	Mixture ratio (wt%)		
		T. vernicifluum	*T. succedanea*	*G. usitata*
1	Mixture lacquer	50	50	0
2	Mixture lacquer	50	0	50
3	Mixture lacquer	0	50	50
4	Pure lacquer	0	100	0
5	Mixture lacquer	9	91	0
6	Mixture lacquer	23	77	0
7	Mixture lacquer	33	67	0
8	Mixture lacquer	50	50	0
9	Pure lacquer	100	0	0