1. Introduction

1.1 Characteristics of lacquer

Oriental lacquer is a reproducible natural product that has been used for thousands of years in Asia. No organic solvent evaporates during the drying process, only water. Because of the self-drying system, natural lacquer is an eco-friendly product that is expected to be useful in the future as a coating material.

Lacquer trees are members of the family Anacardiaceae, which includes more than 73 genera worldwide and approximately 600 species including mango (*Mangifera indica*) and cashew (*Anacardium occidentale*), but most of them grow in the subtropical region of Southeast Asia [1-3]. In general, only a few kinds of lacquer trees that grow in the evergreen forests of East Asia are able to produce lacquer sap.

Lacquer has been used in Asian countries for thousands of years as a durable and beautiful coating material [4-7]. Cultural treasures coated with lacquer have maintained their beautiful surfaces without loss of their original beauty for more than 9000 years [8-10].

Lacquer sap for the manufacture of lacquerware is collected not only in China and Japan but also in Southeast Asia, as shown in Figure 1-1. In Japan, about 10 years after cultivating a lacquer tree, cuts are made in the tree trunk. A white, milky resin seeps out of the wounds, and this sap is collected in a keg. After the lacquer sap has been collected, the tree is left untouched for 3 or 4 days before cuts are again made in the tree to collect more sap. Laccol (MW=348) is the main component of *Rhus succedanea* trees, which grow in Vietnam and Chinese Taiwan, and thitisiol (MW=348) is the main component of *Melanorrhoea (Gluta)* usitata trees, which grow in Thailand and Myanmar [11-13]. All these saps are used as a surface coating for wood, porcelain, and metal wares in Asia.
1.2 Components of lacquer

Lacquer is the sap obtained by tapping lac trees, specifically *Rhus vernicifera* (in Japan, China, and Korea), *Rhus succedanea* (in Vietnam and Taiwan), and *Melanorrhoea* (*Gluta*) *usitata* (in Thailand and Myanmar). The sap from *Rhus vernicifera* comprises a latex material composed of phenol derivatives (60-65%), water (20-25%), plant gum including saccharides (5-7%), water-insoluble glycoproteins (2-5%), and the laccase enzyme (0.1%) [11-13].

Under the microscope, this milky liquid appears to be a collection of water particles in an emulsion. Small particles of water are dispersed in the oily substance called urushiol. Unlike milk, in which fat is dispersed in water, water is dispersed in the urushiol oil in lacquer. The emulsion droplets contain the dissolved laccase enzyme and polysaccharides. It is believed that nitrogenous substances play an important role in forming a stable emulsion of the aqueous component and urushiol.
The composition of lacquer sap has been investigated using gel permeation chromatography (GPC), high performance liquid chromatography (HPLC), mass spectrometry (MS), and nuclear magnetic resonance (NMR), including two-dimensional NMR spectroscopy. Urushiol is a mixture of 3-substituted catechol derivatives having carbon chains with 15 carbons with 0-3 double bonds. The triene side chain of urushiol makes up 60-70% of urushiol [14]. All of these components have been separated and purified. Figure 1-2 shows photographs of urushiol, polysaccharides, glycoprotein, laccase, and stellacyanin obtained from Chinese lacquer sap isolated according to previously reported methods. Procedures utilized for the separation and purification of lacquer components from *Rhus vernicifera* lacquer sap are shown in Figure 1-3 [15].

Fig. 1-2. Photos of lacquer components
Fig. 1-3. Separation of lacquer sap

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1.3 Drying mechanism

The drying mechanism of lacquer sap catalyzed by laccase was first explicated by Kumanotani [16], and the explanation was supplemented and developed by our later studies [17]. The catechol ring of urushiol is first oxidized by laccase to form dimers, trimers, and oligomers, and after the urushiol monomer concentration has decreased to less than 30%, a bridge-construction reaction due to auto-oxidation of the unsaturated side chain occurs. Figure 1-4 shows the laccase-catalyzed oxidation coupling of urushiol [16-17].

![Polymerization mechanism of urushiol catalyzed by laccase](image)

The polymerization of urushiol proceeds through laccase-catalyzed nuclear-nuclear (C-C) coupling. Its detailed mechanism is as follows. During the first step of the dimerization, En-Cu$^{2+}$ oxidizes urushiol to give the semiquinone radical and En-Cu$^+$. During the sap cooking process, the presence of plant gum cause significant foaming, which mixes air and sap during the treatment as well as accelerating the oxidation of Cu$^+$ to Cu$^{2+}$ in the laccase. The reformed En-Cu$^{2+}$ takes part in the repeated oxidation of urushiol. The semiquinone radical formed undergoes a C-C coupling reaction to produce biphenyl dimers, and the urushiol quinone formed through the disproportionation reaction undergoes hydrogen abstraction from the triene side chain of urushiol to give a nucleus-side chain C-C coupling dimer. The polymerization of urushiol may proceed through these types of couplings. However, many and various kinds of reactions may occur in the film-making process. Both enzymatic reaction and auto-oxidation (Figure 1-5) are repeated to form a durable network polymer.
In order to reveal the enzymatic polymerization mechanism of thitsiol, we reinvestigated the dimer structures produced in the initial stage of enzymatic polymerization by using modern techniques including 1H-1H and 1H-13C correlation two-dimensional NMR measurements [18-19]. The structures of thitsiol dimers from *Melanorrhoea (Gluta) usitata* were characterized by means of high-resolution NMR spectroscopy involving two-dimensional NMR measurements using field gradient DQF-COSY, HMQC, and HMBC. Almost all proton and carbon absorptions were assigned. The results showed that the main products of thitsiol dimers catalyzed by laccase are 1,1',2,2'-tetrahydroxy-3,3'-dialkenyl-5,5'-biphenyl, 1,1',2,2'-tetrahydroxy-3,3'-dialkenyl-6,5'-biphenyl, and 1,1',2,2'-tetrahydroxoy-3,4'-dialkenyl-5,5'-biphenyl. The thitsiol dimers are almost all due to nuclear-nuclear (C-C) coupling, which differs from the nuclear-side chain (C-O-C) coupling of urushiol as shown in Figure 1-4 [20].

### 2. Py-GC/MS

Pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) is a comparatively old analytical method (Figure 2-1). It is one of the techniques developed to analyze polymers. It has problems with reproducibility and long analysis times and it was not used very much, though pyrolysis began to be used to analyze natural fibers and synthetic fibers. The technique for combining this pyrolysis method with gas chromatography and a mass spectrometry was reported by Davison in 1954, and it became appreciated in recent years as a significant technique to analyze the three-dimensional network structure. This technique involves high-temperature treatment of the polymer membrane in order to isolate each element of the polymer using the solvent for gas chromatography, and to perform mass spectrometry of the gas chromatography peak at the same time.
The advantage of this technique is the convenience of the device and pretreatment of the analysis sample. In particular, a polymer can be analyzed using a very small amount of sample (0.01-1mg).

The best feature of pyrolysis gas chromatography/mass spectrometry is pyrolysis. The thermal cracking unit can be heated quickly to a high temperature and is directly related to the reproducibility of the analysis performance. The heating in this method is done in a microfurnace (Figure 2-2).

The method involves putting the sample in the inactivated sample holder of the microfurnace, dropping it into the reactor core from the state set in the device, which is filled with helium as the carrier gas using a switch, and then pyrolyzing it. A feature of this technique is that the measurement result is steady because the small capacity keeps the temperature dispersion is comparatively low [21].
2.1 Direct method (single-shot Py-GC/MS)

The easiest Py-GC/MS is a method in which only one heating performs the thermal decomposition, and it is called single shot. The range of temperatures that cause thermal decomposition is 50-1000°C (in the case of the PY-3030). After the sample is thermally decomposed, it was gasified and introduced into a gas chromatography. The gas separated by GC is measured by MS, as shown in Figure 2-3. The advantage of this technique is being able to analyze all components in the original sample by one measurement. This means that the ratio of components in the original solid can be measured.
The decomposition temperature of lacquer film is 500°C. The GC column is a type of dimethyl polysiloxane or phenyl methylpolysiloxane. Because lacquer film has a catechol configuration, its polarity is very high. Therefore, if a very polar column is used, detection will decrease. Moreover, setting the temperature of the oven high enough and using a heat-resistant column are also important because urushiol is undetectable at temperatures lower than 280°C.

2.2 Fragmentation mechanism of lacquer film

The main component of lacquer is urushiol, which is a catechol derivative, and it is polymerized to form a film by the laccase. When a lacquer film is analyzed by Py-GC/MS, mass fragment m/z=108 from alkyl phenol and mass fragment m/z=123 from alkyl catechol will appear as characteristic fragment ions. The fragment ion m/z=108 is the hydrogen attached to the 3-position carbon of the catechol ring that appears due to McLafferty transference. M/z=123 is a fragment ion which the first CH$_2$ from a catechol ring enters another catechol ring, and constitutes a seven-member ring, as shown in Figure 2-4.

![Figure 2-4. Formation mechanism of fragment m/z = 108 and m/z = 123](image)

The pyrolysis GC/MS Chinese lacquer film is shown in Figure 2-5. Many components are detected in the total ion chromatograph, and this is due to the complex structure of the lacquer film and various components contained in a lacquer sap. The ion chromatographs of (A) m/z=108 and (B) m/z=123 are shown in Figure 2-6. It is a graphic chart that is easily intelligible at a glance. The highest peak is the component that has carbon number seven in the side chain. Because the factor that becomes such is cut next to the 8th carbon in which most double bonds exist in urushiol. In the case of urushiol and thitsiol (Figure 2-7), carbon number seven is the most frequent component, but since the position of the double bond changes in laccol, the alkyl phenol of carbon number nine is detected as the greatest peak (Figure 2-8) [22-24].

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Fig. 2-5. Total ion chromatography (TIC) of lacquer film

Fig. 2-6. Ion chromatography of Chinese lacquer film: (A) m/z=108 and (B) m/z=123
2.3 Derivatization method

The principal constituent of Japanese lacquer, urushiol, contains catechol ring. Catechol has two hydroxyl groups of a phenol nature, and because its polarity is high, it tends to adhere to a column. It is said that this leads to a degradation of analytical sensitivity. Adsorption is one reason that the component ratios differ in analysis results. As a method of suppressing
alterations of the component ratio by such adsorption, methylation of the hydroxyl group by tetramethylammonium hydroxide (TMAH) was devised. There are reports of the use of TMAH in analysis of a lignin, which generates a component containing the hydroxyl group during thermal decomposition and is an example of analysis of a polysaccharide [25-30]. TMAH can also be used effectively at the time of the thermal decomposition of Japanese lacquer. The lacquer film and TMAH were combined in the sample cup, and the sample cup was put in the pyrolyzer heated to 500°C.

Scheme 2-1. Methylation reaction of hydroxyl group by TMAH

In a lacquer film, a hydroxyl group replaces a methyl group in a thermal decomposition (Scheme 2-1). The example of a Chinese lacquerware analyzed by this method is shown in Figure 2-9. In this examination, the amount of lacquer film used was 0.75 mg.

Fig. 2-9. Comparison of sensitivity of methylation

When not methylated, the alkylphenol of the carbon number seven should be detected. On the other hand, when it is methylated, 1,2-dimethoxy-3-pentadecylbenzene, from which
urushiol was therefore protected by methylation, was detected. Methylation, even if the amount of lacquer film is small, can reveal urushiol. This method is useful for analysis of cultural properties that can provide only small samples.

2.4 Evolved gas analysis

Evolved gas analysis (EGA) is a method of analyzing the gas emitted during heat is applied to a sample [31-34]. The mechanical configuration characteristically uses a very short column. The column is about 1 m in length, and a fixed zone does not exist. Since many organic macromolecules are decomposed at less than 1000°C, a set of unstring temperatures in the range of 50–1000°C is used. In the case of a lacquer film, the temperature range is set to 50–650°C (Figure 2-10).

Fig. 2-10. Configuration of EGA system

EGA analysis decomposes a lacquer film in three steps (Figure 2-11). When the heat decomposition points were divided into three steps, two were the original peaks of m/z=60
and m/z=108, which is a thermal decomposition peak of urushiol, and one was m/z=123. The first peak of m/z=60 at a lower temperature was short carboxylic acid with various carbon chains. The following peak was considered to be due to the decomposition of sugars. The acetone powder (AP) taken from lacquer sap also was analyzed by EGA, and the peak position of acetone powder was mostly in agreement with the second EGA peak of Japanese lacquer film (Figure 2-12).

![Graph showing EGA of Chinese lacquer film and AP](image)

**Fig. 2-12. EGA of Chinese lacquer film and AP**

### 2.5 Double-shot pyrolysis

An analysis method that can be performed using the results of EGA is double-shot pyrolysis. Double-shot pyrolysis applies heat to the same sample gradually and analyzes only the gas generated in a certain range (Figure 2-13).

![Configuration of double-shot pyrolysis](image)

**Fig. 2-13. Configuration of double-shot pyrolysis**
A sample is placed in a pyrolyzer, and heating is started. The first part of a column is dipped in liquid nitrogen, and the gas chromatograph is not moved. If thermal decomposition occurs at a predetermined temperature, the pyrolyzed sample is removed from the heating block immediately. After raising the sample from the oven, removed the GC column from the liquid nitrogen and then started gas chromatography. Follow this procedure by the number of daylights of a thermal decomposition. In this way, the Py-GC/MS will store a record of each peak of EGA that is attained [35-37].

This technique is convenient to remove only a plasticizer previously added to a sample or to remove a solvent that remains in very small quantity. However, this method cannot be used when a sample reacts with the energy of heating. In the case of a lacquer sap, various additive admixtures (pine drying oil, tar, etc.) may be present. Thus, this technique is very effective when components with clearly different heat decomposition points are present.

3. Application of Py-GC/MS in lacquer analysis

The three kinds of lacquer films analyzed by Py-GC/MS in this section are the lacquer saps from *Rhus vernicifera*, *Rhus succedanea*, and *Melanorrhoea* (*Gluta*) *usitata*. The lacquers were coated on a 70 cm × 40 cm glass plates. They were allowed to polymerize in a humidity-controlled chamber at a relative humidity of 70-90% at 20°C for 12 h, and then removed from the chamber and stored in the open air for 3 years [38].

The pyrolysis-gas chromatography/mass spectrometry measurements were carried out using a vertical microfurnace-type pyrolyzer PY-2010D (Frontier Lab, Japan), an HP 6890 gas chromatograph (Hewlett-Packard), and an HPG 5972A mass spectrometer (Hewlett-Packard). A stainless steel capillary column (0.25 mm i.d. × 30 m) coated with 0.25 μm of Ultra Alloy PY-1 (100% methylsilicone) was used for the separation. The sample (1.0 mg) was placed in the platinum sample cup, and the cup was placed on top of the pyrolyzer at near ambient temperature. The sample cup was introduced into the furnace at 500°C, then the temperature program of the gas chromatograph oven was started. The gas chromatograph oven was programmed to provide a constant temperature increase of 20°C per min from 40° to 280°C, then held for 10 min at 280°C. The flow rate of the helium gas was 18 ml/min. All the pyrolysis products were identified by mass spectrometry. The mass spectrometry ionization energy was 70 eV (EI-mode).

3.1 Pyrolysis of urushiol polymer

The urushiol lacquer film was pyrolyzed at 500°C. The total ion chromatogram (TIC) and mass chromatogram (m/z=320) are shown in Figure 3-1. Although a complex TIC was obtained, the mass chromatogram and mass spectrum revealed that urushiol (MW=320) was the main component of the lacquer.

The pyrolysis products obtained in mass chromatograms and mass spectra of m/z=123 and m/z=108 of urushiol lacquer film are shown in Figure 3-2. 3-Heptylcatechol (C7) and 3-heptylphenol (C7) were detected in the mass chromatogram at m/z=123 and m/z=108, respectively, and had the highest relative intensity.
Fig. 3-1. TIC, mass chromatogram (m/z=320), and mass spectrum of urushiol lacquer film.
Fig. 3-2. Mass chromatograms (m/z=123 and 108) and mass spectra of urushiol lacquer film.
It has been reported that the double bonds of olefins at the $\alpha$- and $\beta$- positions are most susceptible to thermal cleavage [39-40]. Therefore, as shown in Scheme 3-1, the highest yield of 3-heptylcatechol (C7) can be attributed to the preferential cleavage at the $\alpha$-position of the double bonds of the nucleus-14th chain C-O couplings of the urushiol polymers.

Scheme 3-1. Pyrolysis mechanism of urushiol polymer

3.2 Pyrolysis of laccol polymer

A laccol lacquer film was also pyrolyzed at 500°C at the same time as the urushiol lacquer film. The total ion chromatogram and mass chromatogram (m/z=320) are shown in Figure 3-3. Although a complex TIC was obtained, the mass chromatogram and mass spectrum confirmed that laccol (MW=348) was the main component of the lacquer film.

The pyrolysis products obtained in mass chromatograms and mass spectra of m/z=123 and m/z=108 of laccol lacquer film are shown in Figure 3-4. 3-Nonylcatechol (C9) and 3-nonylphenol (C9) were detected in the mass chromatogram at m/z=123 and m/z=108, respectively, and had the highest relative intensity. The detailed Py-GC/MS results of laccol in our laboratory have been previously reported [23].
Fig. 3-3. TIC, mass chromatogram (m/z=348), and mass spectrum of laccol lacquer film
Fig. 3-4. Mass chromatograms (m/z=123 and 108) and mass spectra of laccol lacquer film 

3-Nonyl catechol (MW=236) 

3-Nonylphenol (MW=220)
3.3 Pyrolysis of thitsiol polymer

*Melanorrhoa (Gluta) usitata* is a lacquer tree that grows in Myanmar, Thailand, and Cambodia. The main component of *Melanorrhoa (Gluta) usitata* is thitsiol, which contains 3- and 4-heptadecadienylcatechols as well as a series of α- and β- position.

![Fig. 3-5. TIC and mass chromatograms (m/z=346, 348, 310, 326, 338, 354) of thitsiol lacquer film](image)

The thitsiol lacquer film was pyrolyzed at 500°C. Figure 3-5 shows the TIC and individual mass chromatograms at m/z=346, 348, 310, 326, 338, and 354. Peaks 1, 2, 3, 4, 5, and 6 of the mass chromatograms were identified as 4-heptadecenylcatechol (MW=346), 4-heptadecadienylcatechol (MW=348), 3-(10-phenyldecyl)phenol (MW=310), 3-(10-phenyldecyl)catechol (MW=326), 4-(10-phenyldecyl)phenol (MW=338), and 4-(12-phenyldodecyl)catechol (MW=354), respectively. Because the C-O coupling polymers are terminated with 4-heptadecenylcatechol, these compounds can be formed from such terminal groups.

In the m/z=123 mass chromatograms of the thitsiol lacquer film, a pair of peaks of the 3- and 4-alkylcatechols were detected (figure not shown). The relative intensities of the 3- and 4-heptylcatechols (C7) were the highest in the pyrolysis products of the thitsiol lacquer. The
highest yields of the 3- and 4-heptylcatechols were considered to be mainly due to cleavage at the α-position of the double bonds of the nucleus-8th and 12th chain C=O couplings for the thitsiol polymers. The alkylphenols detected are likely to be the products of pyrolysis of the nucleus-side chain coupling of the thitsiol polymers. Dimerization of the lacquer monomers is considered to proceed through the laccase-catalyzed nucleus-side chain coupling as well as the C-C coupling. The yields of 3-heptylphenol (C7) were the highest, as shown in Figure 3-5. The α- and β-positions of the double bonds of the olefins are susceptible to thermal cleavage so that these highest yields are thought to be produced primarily by cleavage at the α-position of the double bonds of thitsiol, such as the 3- and 4-(8,11-heptadecadienyl)catechols. The detailed Py-GC/MS results of thitsiol in our laboratory have been previously reported [41].

The 3-pentadecylcatechol (MW=320) (urushiol), 3-heptadecylcatechol (MW=348) (laccol), and 4-heptadecylcatechol (MW=348) (thitsiol) are the characteristic pyrolysis products of the three kinds of lacquer films, respectively, as summarized in Table 3-1. Furthermore, the data acquired for the alkylcatechols and alkylphenols in the pyrolysis products also can help to determine the lacquer species.

<table>
<thead>
<tr>
<th>Species of lacquer film</th>
<th>Features of pyrolysis products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Monomer</td>
</tr>
<tr>
<td><em>Rhus vernicifera</em></td>
<td>Urushiol</td>
</tr>
<tr>
<td><em>Rhus succedanea</em></td>
<td>Laccol</td>
</tr>
<tr>
<td><em>Melanorrhoea usitata</em></td>
<td>Thitsiol</td>
</tr>
</tbody>
</table>

Table 3-1. Characteristic pyrolysis products of lacquer films

4. Recent finding on lacquer film using Py-GC/MS

4.1 Identification of lacquer species

As described in Section 3, the main pyrolysis products of urushiol are 3-heptylcatechol and 3-heptylphenol, of laccol are 3-nonylcatechol and 3-nonylphenol, and of thitsiol are 3-heptylcatechol, 3-heptylphenol, and 4-heptylcatechol, respectively. In order to confirm these results, we synthesized urushiol [42], laccol [23], and thitsiol [41] lacquer films and analyzed them by Py-GC/MS measurement.

4.1.1 Synthesis of urushiol lacquer film and analysis by Py-GC/MS

Compound 1, the major component of urushiol, shown in Figure 4-1, was synthesized in good yield via the Witting reaction from a ylide derived from (3E,5Z)-3,5-heptadienyltriphenylphosphonium iodide with 3-(8-oxo-1-octyl) catechol diacetate, using a stepwise procedure based on repeated protection and deprotection of the hydroxyl group of catechol, using the technique we reported previously [43]. The trienyl urushiol compounds 2 and 3 were synthesized in a similar method using ylides derived from (3E,5E)-3,5-heptadienyltriphenylphosphonium iodide and 3E,3,5-heptadienyltriphenylphosphonium iodide, respectively.
Synthesized lacquer films were prepared as follows: 50 mg of compound 1 was added to 10 mg water-isopropyl alcohol (1:1, v/v) containing acetone powder (10 mg), which had been separated as an acetone-insoluble material from \textit{Rhus vernicifera} lacquer sap. The resulting mixture was stirred for about 15 min. The reaction mixture had a viscosity suitable for coating and was coated onto a glass plate and dried in a humidity-controlled chamber with a relative humidity (RH) of 80% at 25-30°C for 10 h. The film was then removed from the chamber and stored in air for 6 months. Films of a single component were prepared. Compounds 2 and 3 were treated in the same manner to obtain the corresponding lacquer films. The films from the synthesized trienyl urushiol components 1, 2, and 3 are called synthesized lacquer films A, B, and C, respectively.

The preparation of natural lacquer was as follows. The sap exuded from a \textit{Rhus vernicifera} lacquer tree in Japan, and composed of the following lipid components: 5% saturated urushiol, 18% monoenyl urushiol, 12% dienyl urushiol, and 65% trienyl urushiol. This lacquer sap was coated onto a glass plate and dried in a humidity-controlled chamber under an RH of 80% at 25-30°C for 10 h. The film was then removed from the chamber and stored in air for 6 months like the synthesized lacquer films.

The three synthesized lacquer films and the natural lacquer film were pyrolyzed at 500°C, and then the resulting pyrolysis products were characterized by GC-MS analysis. The specific ions at m/z 123 and 108 are fragment ions of alkylcatechols and alkylphenols that were produced during the electron ionization process in the mass spectrometer, and the mechanism of the thermal decomposition is shown in Figure 4-2.
Fig. 4-2. Postulated location of urushiol lacquer film pyrolysis and mechanism of formation of m/z=123 and m/z=108 ion species in Py-GC/MS.

The resulting total ion chromatograms (TIC) of the natural and synthesized lacquer films are shown in Figure 4-3. The major components in the TIC peaks were defined as alkanes, alkenes, and alkylbenzenes respectively.

The mass chromatogram of selective scanning of m/z=123 is shown in Figure 4-4. Peaks 1, 2, and 3 were identified as 3-pentylcatechol (M⁺=180), 3-hexylcatechol (M⁺=194), and 3-heptylcatechol (M⁺=208), respectively. Peaks 4 and 5 were observed in only the natural lacquer film, and were identified as the urushiol monomer components 3-pentadecenylcatechol (M⁺=318) and 3-pentadecylcatechol (M⁺=320), based on analysis of their mass spectra, shown in Figure 4-5.

Figure 4-5 shows the mass spectra of compounds giving rise to peaks 1–5 in the selective plotting of m/z=123 ion species in the spectra from the pyrolysis of synthesized and natural lacquer films shown in Figure 4-4. Thus, it is evident from Figure 4-4 that saturated urushiol (peak 5) and monoenuyl urushiol (peak 4) were detected by pyrolysis of the natural lacquer film, but not of the synthesized lacquer films. These urushiols likely produced thermally decomposed fragments from the terminal alkylcatechol and alkenylcatechol side chains of the natural lacquer film. Therefore, it was confirmed that the natural lacquer film has urushiol components with both saturated and monoenuyl side chains, unlike the synthesized lacquer films.
Fig. 4-3. TIC of natural and synthesized lacquer films due to pyrolysis at 500ºC
Fig. 4-4. Selective plotting of ion species (m/z=123) in spectra obtained from TIC of one natural and three synthesized lacquer films
Fig. 4-5. Mass spectra of alkylcatechols from synthesized lacquer film A (peaks 1–3) and natural lacquer film (peaks 4–5) in mass chromatogram (m/z=123)
The highest peak intensity in each mass chromatogram was peak 3, because most urushiol components have a double bond at position 8 of their side chain, and the bond between C7 and C8 is easily thermally decomposed after polymerization as shown in Figure 4-6. The highest peak intensity of *Rhus vernicifera* was 3-heptylcatechol (M*+=208).

![Diagram](https://www.intechopen.com)

_R = C₃H₉₉ alkyl and/or alkenyl group_

_R' = C₁₅H₃₅ alkyl and/or alkenyl group_

Fig. 4-6. Postulated location of lacquer film in thermal decomposition due to pyrolysis

### 4.1.2 Synthesis of laccol lacquer film and analysis by Py-GC/MS

The trienyl and dienyl laccols, compounds 4, 5, and 6, shown in Figure 4-7 were synthesized by a method similar to the synthesis of urushiol described in Section 4.1.1. Compound 4, the major component of laccol, was synthesized via the Witting reaction from a ylide derived from (3E,5E)-3,5-heptadienyltriphenylphosphonium iodide with 3-(8-oxo-1-decyl)catechol diacetate. Compounds 5 and 6 were synthesized from 3Z-heptadienyltriphenylphosphonium iodide and 3E-heptadienyltriphenylphosphonium iodide, respectively.

![Stereo-structure](https://www.intechopen.com)

Fig. 4-8. TIC of natural and synthesized laccol lacquer films due to pyrolysis at 500°C
Fig. 4-9. Selective plotting of ion species (m/z=123) in spectra obtained from TIC of one natural and three synthesized lacquer films.
Fig. 4-10. Mass spectra of peaks 1-5 in the mass chromatogram (m/z=123)
Synthesized and natural laccol lacquer films also were prepared by methods similar to those of urushiol lacquer film described in Section 4.1.1. However, because the laccase activity of *Rhus succedanea* is lower than that of *Rhus vernicifera*, the laccol lacquer films were dried in a humidity-controlled chamber with RH of 90% at 30˚C for 10 h. Then they were removed from the chamber and stored in air for 6 months. The films from the synthesized laccol components 4, 5, and 6 are called synthesized lacquer films D, E, and F, respectively.

The three synthesized laccol lacquer films and one natural *Rhus succedanea* lacquer film were pyrolyzed at 500˚C, and the resulting pyrolysis products were characterized by GC-MS analysis. The specific ions at m/z 123 and 108 are fragment ions of alkylcatechols and alkylphenols that were produced during the electron ionization process in the mass spectrometer, like those of the urushiol lacquer film. The TIC of natural and synthesized laccol lacquer films are shown in Figure 4-8. The major components in the TIC peaks were defined as alkanes, alkenes, and alkylbenzenes, respectively.

The mass chromatogram of the selective scanning of m/z=123 shown in Figure 4-9. Peaks 1, 2, and 3 were 3-heptylcatechol (M*=208), 3-octylcatechol (M*=222), and 3-nonylcatechol (M*=236) respectively. Peaks 4 and 5 were observed in only the natural lacquer film, and were identified as laccol monomer components, 3-heptadecenylcatechol (M*=346) and 3-heptadecylcatechol (M*=348), based on their mass spectra (Figure 4-10).

These laccols were likely produced as thermally decomposed fragments from the terminal alkyl and alkenylcatechol of the natural *Rhus succedanea* lacquer film. Therefore, the natural lacquer sap has laccol components with both saturated and monoenoyl side chains, but the synthesized laccols did not. This was the same result as that of the natural lacquer film from *Rhus vernicifera*. The highest peak intensity was peak 3 in each mass chromatogram because most laccol components have a double bond at position 10 of their side chain, and the bond between C9 and C10 is easily thermally decomposed after polymerization. This result was different from that of the lacquer film from *Rhus vernicifera*, which has a double bond at position 8 of its side chain. The highest peak intensity of *Rhus vernicifera* was 3-heptylcatechol (M*=208), of *Rhus succedanea* was 3-nonylcatechol (M*=236).

### 4.1.3 Synthesis of thitsiol lacquer film and analysis by Py-GC/MS

The main component of thitsiol, 3-(10-phenyldecyl)catechol, was synthesized by the reaction of dimethyl ether with catechol and 1-phenyl-10-iododecane with n-BuLi, followed by

$$\text{HO(CH}_2\text{)}_{10}\text{OH} \rightarrow \text{HO(CH}_2\text{)}_{10}\text{Br} \rightarrow \text{HO(CH}_2\text{)}_{10}\text{Ph} \rightarrow \text{I(CH}_2\text{)}_{10}\text{Ph}$$

$$\text{n-BuLi, Br_3}$$

**Fig. 4-11. Synthesis of 3-(10-phenyldecyl)catechol**
deprotection of the hydroxyl groups of catechol, as shown in Figure 4-11. The detail experimental process can be found in the literature (3 and 4).

The preparation of synthesized thitsiol lacquer films is as follow: 50 mg 3-(10-phenyldecyl)catechol was added to 50 mg of a water-isopropyl alcohol mixture (1:1,v/v) containing 20 mg acetone powder obtained from a natural Melanorrhoea (Gluta) usitata lacquer sap. The resulting mixture was stirred for about 15 min, and then applied to a glass sheet and dried in a humidity-controlled chamber with a RH of 90% at 30°C for 10 h. The film was then removed from the chamber and stored in air for 6 months. The natural lacquer film also was prepared by the same method.

The synthesized thitsiol lacquer films and a natural Melanorrhoea (Gluta) usitata lacquer film were pyrolyzed at 500°C, and then the resulting pyrolysis products were characterized by GC-MS analysis. Figure 4-12 shows the TIC of the natural and synthesized lacquer films. The main pyrolysis products of the natural lacquer film were identified as alkanes, alkenes, alkylbenzenes and alkenylbenzenes by the mass spectra. On the other hand, alkanes and alkenes were not detected in the TIC of the synthesized lacquer film because the alkanes and alkenes were derived from 3- or 4-alkenylcatechols contained in the natural lacquer sap. Each peak in TIC is a pair of peaks of saturated and unsaturated components having one double bond in the termination. It was considered that the alkanes and alkenes were formed by decomposition of the terminal of the lipid components in the polymer.
Figure 4-13 is the mass chromatograms (m/z=123) of natural and synthesized thitsiol lacquer films. Alkylcatechol was detected in the mass chromatogram of the natural lacquer film, and detected as a pair peak of 3-alkylcatechol and 4-alkylcatechol. Due to the analysis of each mass spectrum, the detailed assignment was as follows: ①: 3-methylcatechol, 1: 4-methylcatechol; ②: 3-ethylcatechol, 2: 4-ethylcatechol; ③: 3-propylcatechol, 3: 4-propylcatechol; ④: 3-butylcatechol, 4: 4-butylcatechol; ⑤: 3-pentylcatechol, 5: 4-pentylcatechol; ⑥: 3-hexylcatechol, 6: 4-hexylcatechol; ⑦: 3-heptylcatechol, 7: 4-heptylcatechol; ⑧: 3-octylcatechol, 8: 4-octylcatechol; 9: 3-pentadecylcatechol; 10: 3-(10-phenyldecyl)catechol.

Fig. 4-13. Mass chromatogram (m/z=123) of natural and synthesized films

Natural lacquer film

Synthesized lacquer film

Fig. 4-14 shows the mass spectra of pair of peaks ⑥-6 and ⑦-7. These components were derived from 3-alkylcatechol or 4-alkylcatechol contained as monomeric components in Melanorrhoea (Gluta) usitata. On the other hand, alkylcatechol was not detected in the mass chromatogram of the synthesized lacquer film because the synthesized lacquer film included no alkylcatechols as monomeric components. The side chain of the polymerized o-alkylcatechol was difficult to decompose by heating because o-alkylcatechol is not polymerized at the side chain by auto-oxidation like a fatty acid. Therefore, alkylcatechol was not detected in the mass chromatogram. However, 3-(10-phenyldecyl)catechol was detected as a monomer. The highest pair-peaks intensity of Melanorrhoea (Gluta) usitata was 3-heptylcatechol and 4- heptylcatechol (M+=208, peaks ⑦ and 7 in Figure 4-13).
Fig. 4-14. Mass spectra of pair of peaks of ն-6 and շ-7.

Peak 6

Peak 7
The synthesized lacquer films and corresponding natural lacquer films were characterized using Py-GC/MS. The saturated and monoenoxy components were detected in the natural *Rhus vernicifera* and *Rhus succedanea* lacquer films, respectively, but not in the synthesized lacquer films. However, alkoxyphenols, alkenyloxyphenols, alkanes, and alkenes having longer carbon chains than the side chains of the synthesized lacquers were detected by the Py-GC/MS analysis. Comparing the peak intensity of the mass chromatograms with that of *Rhus succedanea*, *Rhus vernicifera*, and *Melanorrhoea (Gluta) usitata* lacquer films showed that the highest peak of *Rhus vernicifera* represented the C7 components (heptyl catechol and heptyl phenol), and the highest peak of *Rhus succedanea* represented the C9 components (nonylcatechol and nonylphenol) due to a double bond in position 10 of its side chain of laccol. On the other hand, a pair of peaks of 3-alkylcatechol and 4-alkylcatechol was detected in the *Melanorrhoea (Gluta) usitata* lacquer film. The highest pair peaks were 3-heptyl catechol and 4-heptyl catechol due to the side chain attached in position 3 and/or position 4 of catechol ring of thisiol.

### 4.2 Identification of ancient lacquerware

Py-GC/MS is a powerful and versatile technique to identify Oriental lacquers as described above. In this section, we describe analysis of several ancient lacquerwares by Py-GC/MS, and compared with the results of natural lacquer films to determine the kind of lacquer.

#### 4.2.1 Ryukyu lacquerware

We have analyzed six kinds of Ryukyu lacquerware by Py-GC/MS to determine the lacquer source [44]. Six pieces of lacquer belonging to Urasoe Art Museum are summarized in Table 4-1, and the photos of each lacquerware object are shown in Photo 4-1. Each sample was removed from the ancient lacquerware objects during restoration. All pieces of Ryukyu lacquerware in Table 4-1 were analyzed by pyrolysis-gas chromatography/mass spectrometry at 500°C.

<table>
<thead>
<tr>
<th>No.</th>
<th>Collection method</th>
<th>Art object</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Naturally flaked off</td>
<td>Black lacquer wood box with <em>Raden</em> (43)</td>
</tr>
<tr>
<td>2</td>
<td>Naturally flaked off</td>
<td>Black lacquer table box with <em>Raden</em> (66)</td>
</tr>
<tr>
<td>3</td>
<td>Naturally flaked off</td>
<td>Black lacquer box with <em>Hakue</em> (220)</td>
</tr>
<tr>
<td>4</td>
<td>Naturally flaked off</td>
<td>Black lacquer box with <em>Hakue</em> (416)</td>
</tr>
<tr>
<td>5</td>
<td>Collection during restored</td>
<td>Black lacquer box with <em>Raden</em> (26)</td>
</tr>
<tr>
<td>6</td>
<td>Collection during restored</td>
<td>Red lacquer fabric bowl with <em>Hakue</em> (100)</td>
</tr>
</tbody>
</table>

Table 4-1. Samples used for pyrolysis
Photo 4-1. Six lacquer objects belonging to Urasoe Art Museum

Figure 4-15 shows the TIC and mass chromatogram (m/z=320, m/z=123, m/z=108) of Sample 2. The peak at the retention time of 14.326 min (m/z=320) is urushiol, at 10.038 min (m/z=123) is 3-heptylcatechol, and at 9.139 min (m/z=108) is 3-heptylphenol respectively. The mass spectra are shown in Figure 4-16. Samples 1, 4, and 5 showed TIC, mass chromatograms, and mass spectra similar to that of Sample 2, suggested that these four lacquerwares were made from *Rhus vernicifera*. The TIC and mass chromatogram of Sample 3 are shown in Figure 4-15, and the mass spectrum is shown in Figure 4-16. The results showed that the peak at the retention time of 16.072 min (m/z=348) is laccol, at 11.105 min (m/z=123) is 3-nonyl catechol, and at 10.282 min (m/z=108) is 3-nonylphenol. Sample 6 produced the same pyrolysis results as Sample 3, suggesting that these two lacquerwares were made from *Rhus succedanea*. The pyrolysis products of the six samples are summarized in Table 4-2.

The Py-GC/MS results of Ryukyu ancient lacquerware confirmed that four lacquerware objects belonging to the Urasoe Art Museum were made from lacquer sap of *Rhus vernicifera* and the other two were made from lacquer sap of *Rhus succedanea* lacquer sap. Because Py-GC/MS analysis revealed the answer to the question of what kind of lacquer sap was used to produce Ryukyu lacquerware, the procurement source and production system of the materials of Ryukyu lacquerware could be clarified, and will be very useful in the conservation and restoration of other valuable ancient lacquer ware.
Fig. 4-15. TIC, mass chromatograms (m/z=320, 123, and 108) of sample 2.
Fig. 4-16. Mass spectra of sample 2

3-Heptylcatechol (MW=208)

3-Heptylphenol (MW=192)

Urushiol (MW=320)
Table 4-2. Pyrolysis products of Ryukyu lacquer films and their species

<table>
<thead>
<tr>
<th>No.</th>
<th>Lacquer species</th>
<th>Pyrolysis products</th>
<th>Monomer</th>
<th>Alkylcatechol</th>
<th>Alkylphenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><em>Rhus vernicifera</em></td>
<td>Urushiol</td>
<td>3-heptylcatechol</td>
<td>3-heptylphenol</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td><em>Rhus vernicifera</em></td>
<td>Urushiol</td>
<td>3-heptylcatechol</td>
<td>3-heptylphenol</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td><em>Rhus succedanea</em></td>
<td>Laccol</td>
<td>3-nonyl catechol</td>
<td>3-nonyl phenol</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td><em>Rhus vernicifera</em></td>
<td>Urushiol</td>
<td>3-heptylcatechol</td>
<td>3-heptylphenol</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td><em>Rhus vernicifera</em></td>
<td>Urushiol</td>
<td>3-heptylcatechol</td>
<td>3-heptylphenol</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td><em>Rhus succedanea</em></td>
<td>Laccol</td>
<td>3-nonyl catechol</td>
<td>3-nonyl phenol</td>
<td></td>
</tr>
</tbody>
</table>

4.2.2 Other ancient lacquerware

An ancient lacquer film was obtained from the surface of a wooden dish extracted from an excavation site that dates back to the 17th–18th century A.D. at *Kinenkanmae Iseki* on the campus of Meiji University in Tokyo, Japan, called Sample 1. A *Nanban* lacquer film from the 17th century A.D., called Sample 2, and an old lacquer film imported from an Asian country during the 17th–18th century A.D., called Sample 3, were obtained from the surface of wooden crafts objects [38]. Pieces of lacquer taken from a four-eared jar that is a Japanese National Important Cultural Property found in 16th–17th century Kyoto ruins, called Sample 4, was a piece of lacquer obtained from the side of the vessel [22].

The *Baroque* and *Rococo* lacquer films were obtained from the wood surfaces of the Rococo church St. Alto in Altomunster, Munich, Germany, identified as Samples 5 [38]. It is sometimes extremely important to determine whether objects that are claimed to be lacquerware are actually created from lacquer sap or other resins. Whether an object is lacquerware can be precisely determined by the presence of urushiol, laccol, or thitsiol with alkylcatechols and alkylphenols using Py-GC/MS.

The TIC and mass chromatograms of m/z=320 of Sample 1 are shown in Figure 4-17. Urushiol, 3-pentadecylcatechol (MW=320), was identified as the monomer of the lacquer film based on the mass spectrum and retention time. This result was compared to those of the three types of Oriental lacquers. 3-Pentadecylcatechol of MW=320 is the saturated urushiol component, which is the monomer of the *Rhus vernicifera* lacquer. The monomers of the *Rhus succedanea* lacquer are laccol components such as 3-pentadecylcatechol of MW=348. This was not detected in the Sample 1 except for the 3-pentadecylcatechol of MW=320. The monomer of *Melanorrhoea usitata* lacquer is thitsiol, which has saturated and monoenyl side chains, such as 4-heptadecylcatechol (MW=348) and 3- and 4-(o-phenylalkyl) phenols and catechols, and these components, except for the 3-pentadecylcatechol of MW=320, were not detected in the Sample 1. It was concluded that the Sample 1 lacquer was made from *Rhus vernicifera* lacquer sap.
The TIC and mass chromatograms of m/z=60, m/z=123, and m/z=108 from the pyrolysis products of the Sample 2 are shown in Figure 18. The mass chromatograms of m/z=60 indicated that the Sample 2 lacquerware included a drying oil [45], which was added to retard the rate of hardening and affected the physical properties of the film. The mass chromatograms of m/z=108 and m/z=123 of the pyrolysis products of the lacquerware are
also shown in Figure 4-18. The greatest number of peak were from 3-heptylphenol (C7) and
3-heptylcatechol (C7), as revealed by the mass spectra. It was concluded that the Sample 2
lacquer was made from *Rhus vernicifera* lacquer sap. Urushiol was not detected because the
surface of the Sample 2 lacquerware was oxidized by oxygen and light. A type of wax was
detected in the mass spectrum of the TIC from the pyrolysis products. It is considered that
the wax was used to polish the surface of the lacquerware.

Fig. 4-18. Pyrolysis data of Sample 2 lacquer film
The TIC and mass chromatograms of m/z=123 and m/z=108 for the pyrolysis products of the Sample 3 are shown in Figure 4-19. Alkylcatechols and alkylphenols were detected in the mass chromatograms. The greatest number of peaks was due to the 3- and 4-nonylcatechols (C9) and 3-heptylphenol (C7), as determined from the mass spectra. It was concluded that the Sample 3 lacquerware was produced using *Melanorrhoea (Gluta) usitata* lacquer sap. Thitsiol was not detected in the pyrolysis data because the surface of the lacquerware was oxidized by oxygen and exposure to light. From the TIC and mass spectra of the pyrolysis products, a type of wax was detected. The wax was determined to be a type of beeswax, as revealed by the mass spectra. The beeswax was used to protect and polish the surface of the lacquerware.

![Fig. 4-19. Pyrolysis data of Sample 3](image-url)
The TIC and mass chromatograms of m/z=123 and m/z=108 for the pyrolysis products of Sample 4 are shown in Figure 4-20. The peak at the retention time of 17.3 min (m/z = 123, peak 1) is 3-(10-phenyldecyl)catechol, and at 20.4 min (m/z = 123, peak 2) is 3-(10-phenyldodecyl)catechol, according to the results of analysis of the mass chromatogram. It was concluded that the Sample 4 lacquer was made from *Melanorrhoea (Gluta) usitata* lacquer sap.

![Fig. 4-20. Mass chromatograms of Sample 4](image-url)

Figure 4-21 shows the Py-GC/MS products of the Sample 5 (Baroque and Rococo) lacquer films. Lacquer components were not detected in the TIC on the mass chromatograms of the alkylcatechols of m/z=123 and alkylphenols of m/z=108 of the pyrolysis products. Monoterpene components and sesquiterpene components were detected in the pyrolysis products of both lacquerwares. It was concluded that the lacquerwares were made from natural resins, but the pyrolysis products of the Baroque and Rococo lacquer and natural resins using this method were not clear.

It was concluded that 3-pentadecylcatechol (MW=320) (urushiol), 3-heptadecylcatechol (MW=348) (laccol), and 4-heptadecylcatechol (MW=348) (thitsiol) are the main products of the pyrolysis of *Rhus vernicifera*, *Rhus succedanea*, and *Melanorrhoea usitata*, respectively. Compared with the results of the natural lacquer film, the ancient lacquer film (Sample 1) and Nanban lacquer film (Sample 2) were assigned to *Rhus vernicifera*, both the old lacquerware objects imported from an Asian country (Sample 3) and the lacquer taken from a four-eared jar that is a Japanese National Important Cultural Property obtained from 16th–17th century Kyoto ruins (Sample 4) were assigned to *Melanorrhoea (Gluta) usitata*. However, although they were also called “lacquer,” the Baroque and Rococo (Sample 5) lacquer film were identified as being made from a natural resin. The pyrolysis products clearly showed a good correspondence to the components of the lacquer sap.
5. Conclusion

This chapter describes the chemical properties of lacquer saps and films that were analyzed by pyrolysis-gas chromatography/mass spectrometry measurement. It was revealed that the advanced Py-GC/MS analytical method is useful for identifying and evaluating the lacquer components and the origin of lacquer species. Py-GC/MS is a well-known method applied to various areas. Due to its ease of control, speed of analysis, and good reproducibility, the Py-GC/MS method not only can be applied to lacquer films, organic coatings, and other materials that cannot be dissolved in solvents, but also to discriminate between lacquer and other resins for the conservation or restoration of lacquerware.

6. References


Progress in agricultural, biomedical and industrial applications' is a compilation of recent advances and developments in gas chromatography and its applications. The chapters cover various aspects of applications ranging from basic biological, biomedical applications to industrial applications. Book chapters analyze new developments in chromatographic columns, microextraction techniques, derivatisation techniques and pyrolysis techniques. The book also includes several aspects of basic chromatography techniques and is suitable for both young and advanced chromatographers. It includes some new developments in chromatography such as multidimensional chromatography, inverse chromatography and some discussions on two-dimensional chromatography. The topics covered include analysis of volatiles, toxicants, indoor air, petroleum hydrocarbons, organometallic compounds and natural products. The chapters were written by experts from various fields and clearly assisted by simple diagrams and tables. This book is highly recommended for chemists as well as non-chemists working in gas chromatography.

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