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# The Analysis of Urushi by Pyrolysis-Gas Chromatography and Mass Spectrometry

## 1. Introduction

The identification of oriental lacquer types in ancient coatings is very important for conservation and restoration studies. Therefore, various examples of ancient lacquerware were analyzed by means of pyrolysis-gas chromatography and mass spectrometry, and the results were compared with the characteristics of natural lacquer films.

Oriental lacquer is produced from the sap of the lacquer tree, specifically *Rhus vernicifera* in Japan and China, *Rhus succedanea* in Vietnam and Taiwan and *Melanorrhoea usitata* in Thailand and Burma. The saps are mainly used as a surface coating for wood, porcelain and metalware in Asian countries. The sap of *Rhus vernicifera* is a water/oil type emulsion. The oily portion consists of about 60 % urushiol. The sap consists of about 30 % water, about 10 % water soluble plant gum, such as mono-, oligo-, and polysaccharides, and water-insoluble glycoproteins as shown in table 1. The sap also contains small amounts of enzymes such as peroxidase and stellacyanin, but most important, *Rhus laccase*.

To prepare the lacquer sap for the actual coating material, the sap is stirred in an open vessel at room temperature for about one or two hours until the water content is reduced to about 2 %. The temperature cycle must be carefully controlled in order to retain the activity of the enzymes. At this point the sap has become clear, has changed in color, and has increased in viscosity. The resultant liquid, known as *Kurome* lacquer, consists of urushiol, oligo urushiol, and a small amount of water, and is ready for application. The unprocessed sap is sometimes used as the base coat of the substrate and the treated sap *(Kurome urushi)* is applied as the top coat. The lacquer is now applied to the substrate, dried for one day at 20 °C and at a relative humidity of 70 %. The curing of the urushiol is due to oxidation of the urushiol and other components of the raw lacquer by the enzymes present in the sap. Laccase is the most important enzyme for the polymerization of urushiol.

Table 1. Constituents of the sap from *Rhus vernicifera*

| Component | Content (%) |
|---|---|
| Urushiol | 55-65 |
| Glycoproteins | 2-3 |
| Polysaccharides | 5-7 |
| Laccase | < 0.1 |
| Water | 20-30 |

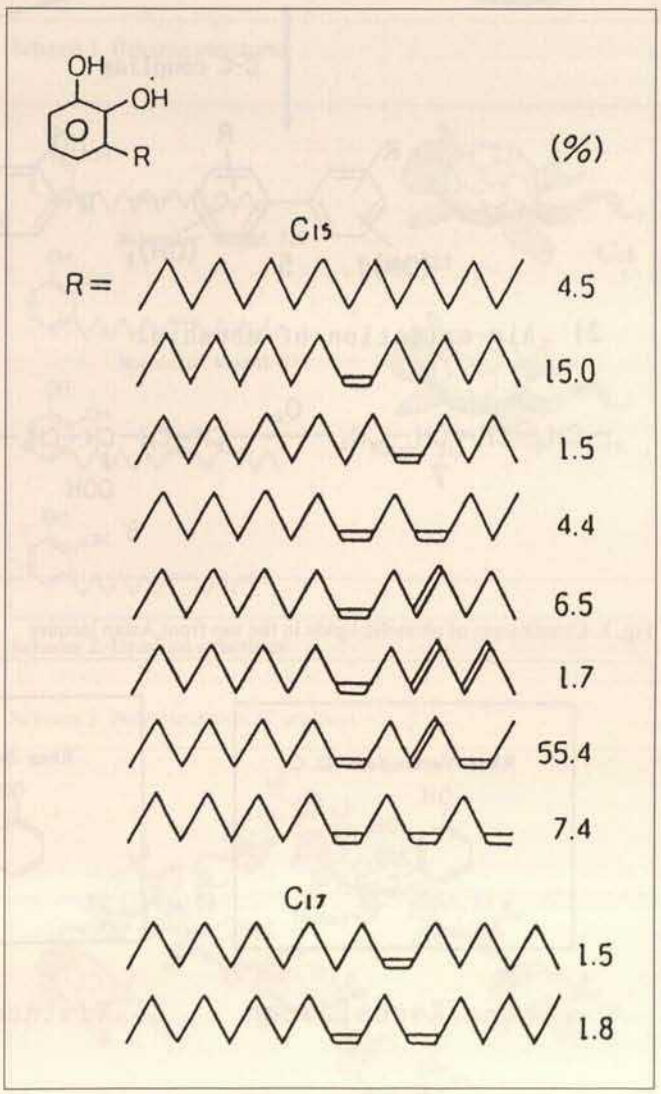



Fig. 1. Constituents of urushiol

Urushiol from *Rhus vernicifera* consists of about 60–70 % of a mixture of catechol substituted in the 3-position with a C-15 hydrocarbon side chain. About 60 % are trienes, about 20 % are monoenes and some dienes are also present as shown in figure 1. The average number of olefins in the side chain of urushiol is 2–2.5. The composition of the urushiol may vary depending on the growing conditions of the lacquer tree and on variations in the seasons. Constituents of the Japanese and Chinese lacquer urushiols appear to be the same. The major constituents of *Rhus vernicifera* are the olefinic isomers, which are the important constituents for the high degree of polymerization of urushiol by the action of *Rhus laccase* in the film-making process or drying process from the sap or lacquer.

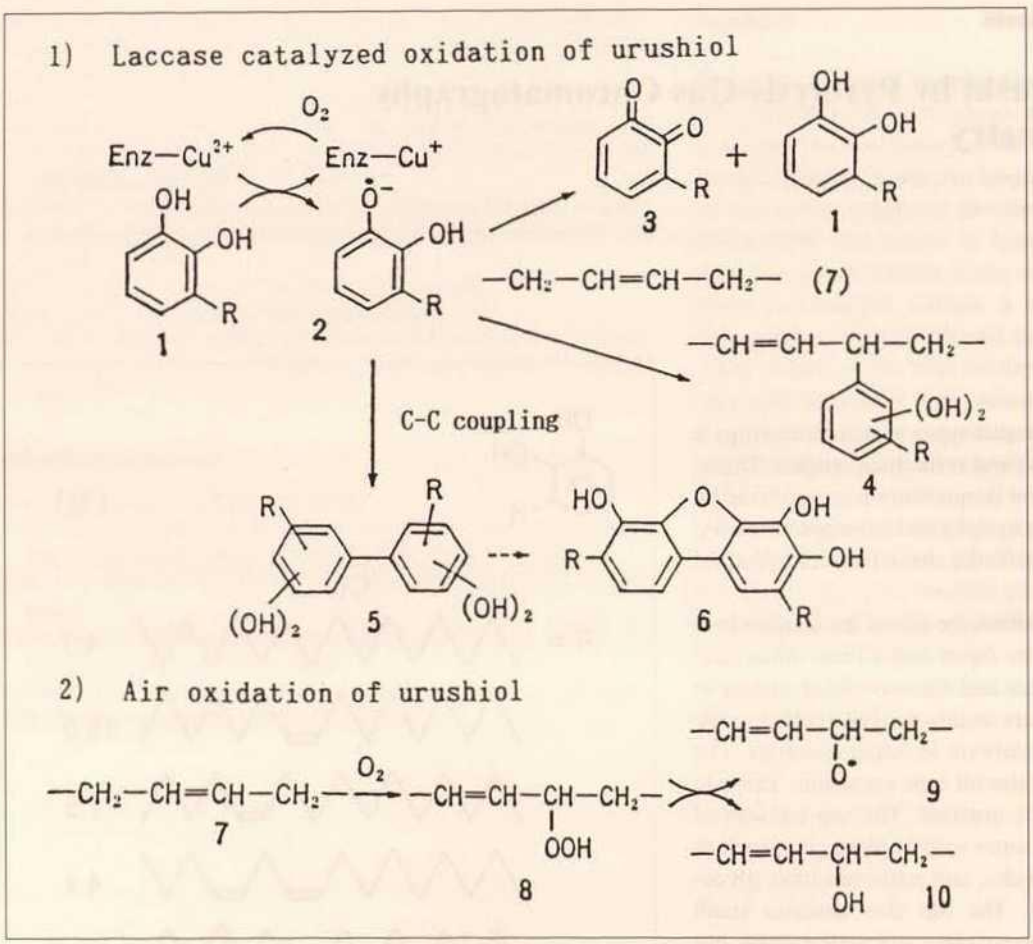
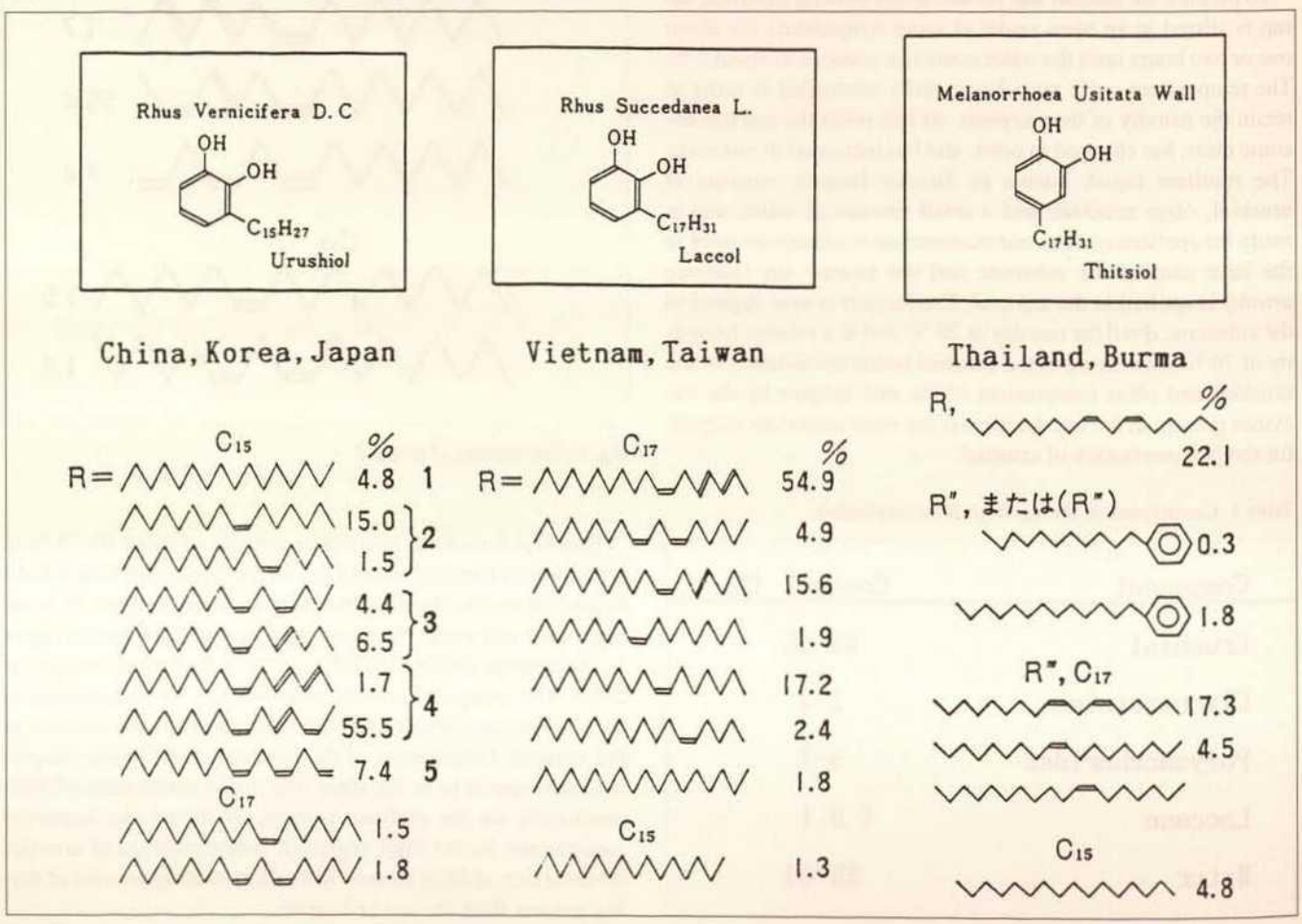



Fig. 2. Polymerization mechanisms of urushiol

Fig. 3. Constituents of phenolic lipids in the sap from Asian lacquer



The dimerization of urushiol proceeds through the laccase-catalyzed C-C and C-O coupling reactions. The detailed mechanism has been reported by Professor Kumanotani. The reaction scheme for the laccase-catalyzed oxidation and air oxidation of urushiol is shown in figure 2. The polymerization probably proceeds through these types of couplings. Finally, a tough and brilliant film is produced.

As already indicated, there are three kinds of oriental lacquers: *Rhus vernicifera* from Japan and China, *Rhus succedanea* from Vietnam and Taiwan, and *Melanorrhoea usitata* from Thailand and Burma as shown in figure 3. The saps of the oriental lacquer latex are composed of phenol derivatives, water, plant gum, glycoprotein, and the laccase enzyme. The phenol derivatives of the *Rhus vernicifera* lacquer are urushiol, those of the *Rhus succedanea* lacquer are laccol, and those of the *Melanorrhoea usitata* lacquer are thitsiol.

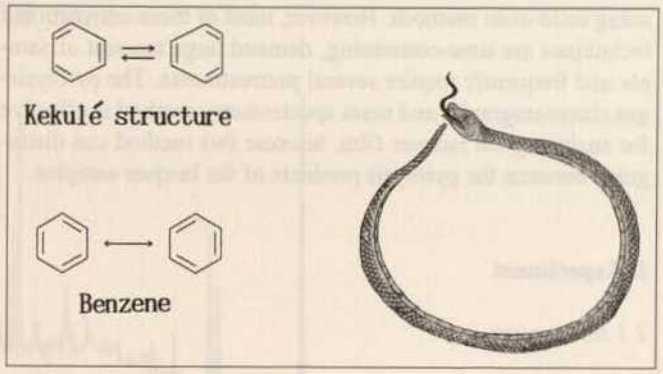
Although chemists usually use chemical symbols and chemical formulas to represent chemical structures, chemical equations and chemical reaction schemes, these formulas are generally too complicated for conference presentation such as this, which are attended by researchers from various fields.

The formulation of the structure was developed for us in 1865 by the German chemist August Kekulé. He dreamt of a snake that was curled in a circle and bit its tail. Applying the image in his dream to the structure of benzene, he proposed that benzene had a cyclic structure, with the ends of the chain bending around to form a hexagon (scheme 1).

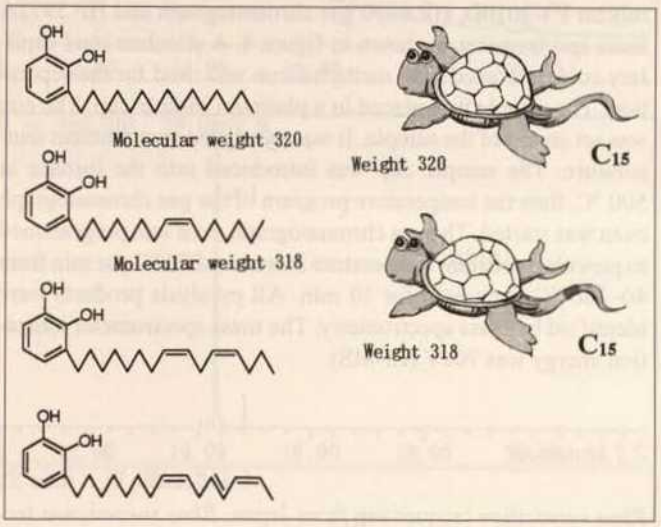
In Japan, the benzene ring is often represented by a turtle shell. The patterns on turtle shells look like benzene rings. An old Japanese proverb says that 'a crane lives a thousand years, and a turtle lives ten thousand years.' Both animals are symbols for long life. Similarly, lacquer has been used for more than 5000 years in Asia. In the Shosoin temple in Japan, a great number of cultural treasures that are coated with oriental lacquer are exhibited, which have all been preserved for more than a thousand years without having lost their original elegance and beauty.

In this paper we will use the sketch of a turtle instead of the chemical formula of the benzene ring. Urushiol is a benzene derivative with two hydroxyl groups and a long side chain. Urushiol of a white turtle has two special hands for the two hydroxyl groups and a long tail for the side chain as shown in scheme 2. The molecular weight of urushiol is 320, which is the weight of the turtle. The length of the long tail for the side chain is carbon 15. The unsaturated side chain and two hydroxyl groups have a very high oxidative reactivity. They are involved in the enzymic and air oxidative polymerization. A turtle forms a double bond by grasping the tail of another turtle using his hand. The C-C double bond at the tail of the turtle is easily caught by other turtles. The polymerization of urushi is represented by several turtles linked together, hand in hand or tail in hand (scheme 3). The striped turtle represents laccol that has two special hands for hydroxyl groups and a long tail for the side chain. The molecular weight of laccol is 348, which is the weight of the striped turtle. The length of the long tail for the side chain is carbon 17. The dotted turtle represents thitsiol and has two special hands for the hydroxyl groups and a long tail for the side chain. The molecular weight of thitsiol is 348, which is the weight of the dotted turtle. The length of the long tail is carbon 17, and it winds around the side (scheme 4).

Urushi films are a cross-linked polymer. Because the lacquer film is insoluble in most solvents, it has only been analyzed

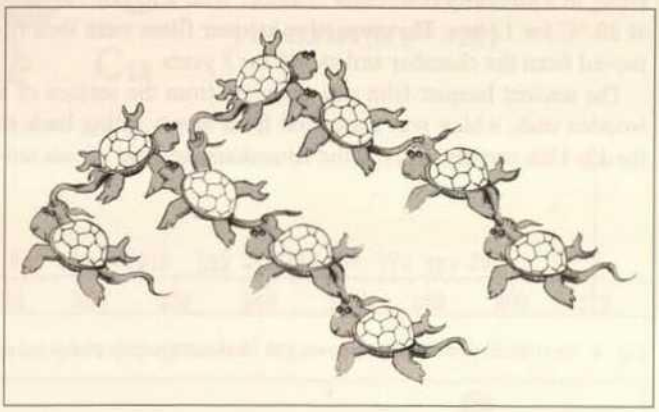



Scheme 1. Benzene structures

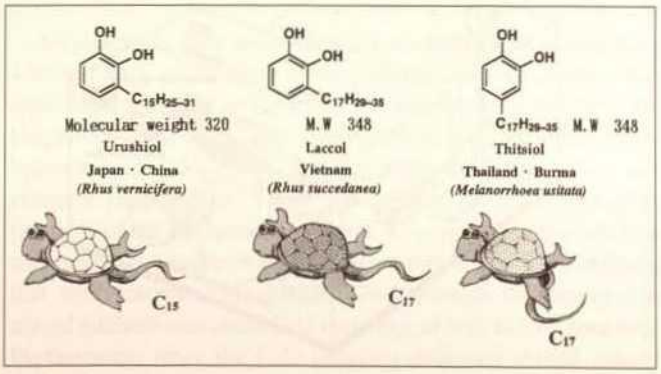



Scheme 2. Urushiol structures

Scheme 3. Polymerization of urushiol



Scheme 4. The typical phenolic lipid of oriental lacquer saps



using solid-state methods. However, most of these conventional techniques are time-consuming, demand large amount of sample and frequently require several pretreatments. The pyrolysis-gas chromatography and mass spectrometry method is effective for analyzing the lacquer film, because this method can distinguish between the pyrolysis products of the lacquer samples.

## 2. Experiment

### *2.1 Instruments*

Pyrolysis-gas chromatography and mass spectrometry measurements were carried out using a vertical micro furnace-type pyrolyzer PY-2010D, HP 6890 gas chromatograph and HP 5972A mass spectrometer as shown in figure 4. A stainless steel capillary column coated with methylsilicon was used for the separation. The sample was placed in a platinum sample cup. The cup was set on top of the sample. It was pyrolyzed 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 40–280 °C, then held for 10 min. All pyrolysis products were identified by mass spectrometry. The mass spectrometer ionization energy was 70eV (EI-MS).

### *2.2 Materials*

*Rhus vernicifera* lacquer sap from Japan, *Rhus succedanea* lacquer sap from Vietnam and *Melanorrhoea usitata* lacquer sap from Burma were treated using the traditional Nayashi and Kurome methods, and coated on glass plates followed by hardening in a humidity controlled chamber with a RH of 70–90 % at 20 °C for 12 hrs. The respective lacquer films were then removed from the chamber and stored for 3 years.

The ancient lacquer film was obtained from the surface of a wooden dish, which was excavated from layers dating back to the 17–18th century A. D. at the Kinenkanmae iseki on our university campus in the Tokyo prefecture of Japan. A *namban* lacquer film from the 17th century A. D. and an old lacquer film exported from an Asian country during the 17–18th century A. D. were obtained from the surface of the wooden crafts.

The Rococo lacquer film was obtained from the wooden surface of the Rococo Church St. Alto in Altomunster, near Munich, Germany.

## 3. Results and Discussion

### *3.1 Pyrolysis-gas chromatography and mass spectrometry of* Rhus vernicifera *and* Rhus succedanea *lacquer films*

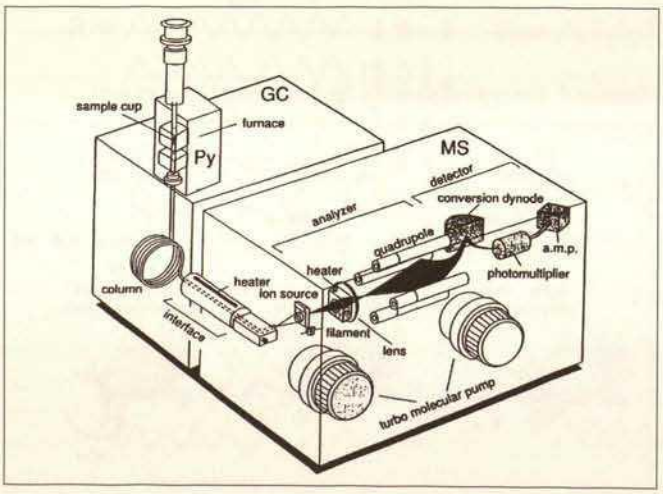
*Rhus vernicifera* and *Rhus succedanea* lacquer films were pyrolyzed at 500 °C. The total ion chromatogram (TIC) and mass chromatogram (m/z 320) of the *Rhus vernicifera* lacquer are shown in figure 5. Peak u-1 was identified as the urushiol (MW 320) based on the mass spectrum. The white turtle representing urushiol is found in the pyrolysis products. The TIC and mass chromatogram of m/z 320 and 348 from the *Rhus succedanea* lacquer film are shown in figure 6. Peak l-1 was identified as a striped turtle for laccol (MW 348) by the mass spectrum. Laccol is a typical component of Vietnamese lacquer.

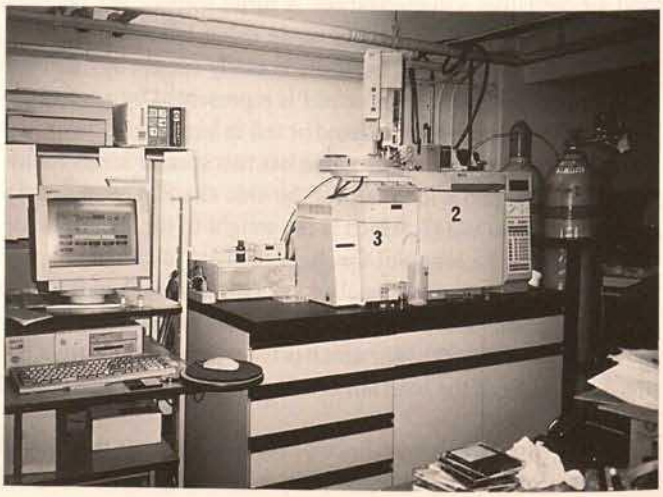
Urushiol (MW 320) was detected in both the *Rhus vernicifera* and the *Rhus succedanea* lacquer films. In contrast, laccol (MW 348) was detected only in the *Rhus succedanea* lacquer film. The pyrolysis products clearly show a good correlation with the constituents of the respective lacquer saps.

Alkylcatechols and alkylphenols are mainly observed as the thermally decomposed components from the terminal alkylcatechol-side chains of the lacquer films. Based on the results for these two specimen, it was possible to differentiate between the species.

Alkylcatechols were detected in the mass chromatograms (m/z 123) at 500 °C of the *Rhus vernicifera* and *Rhus succedanea* lacquer films as shown in figure 7. The alkylcatechols that have the longest side chain are the pentadecylcatechols in the *Rhus vernicifera* lacquer film, whereas those in the *Rhus succedanea* lacquer film are heptadecylcatechols. In addition,

Fig. 4. Analytical system of pyrolysis-gas chromatography and mass spectrometry. 1: Pyrolyzer, 2: Gas chromatograph, 3: Mass spectrometer



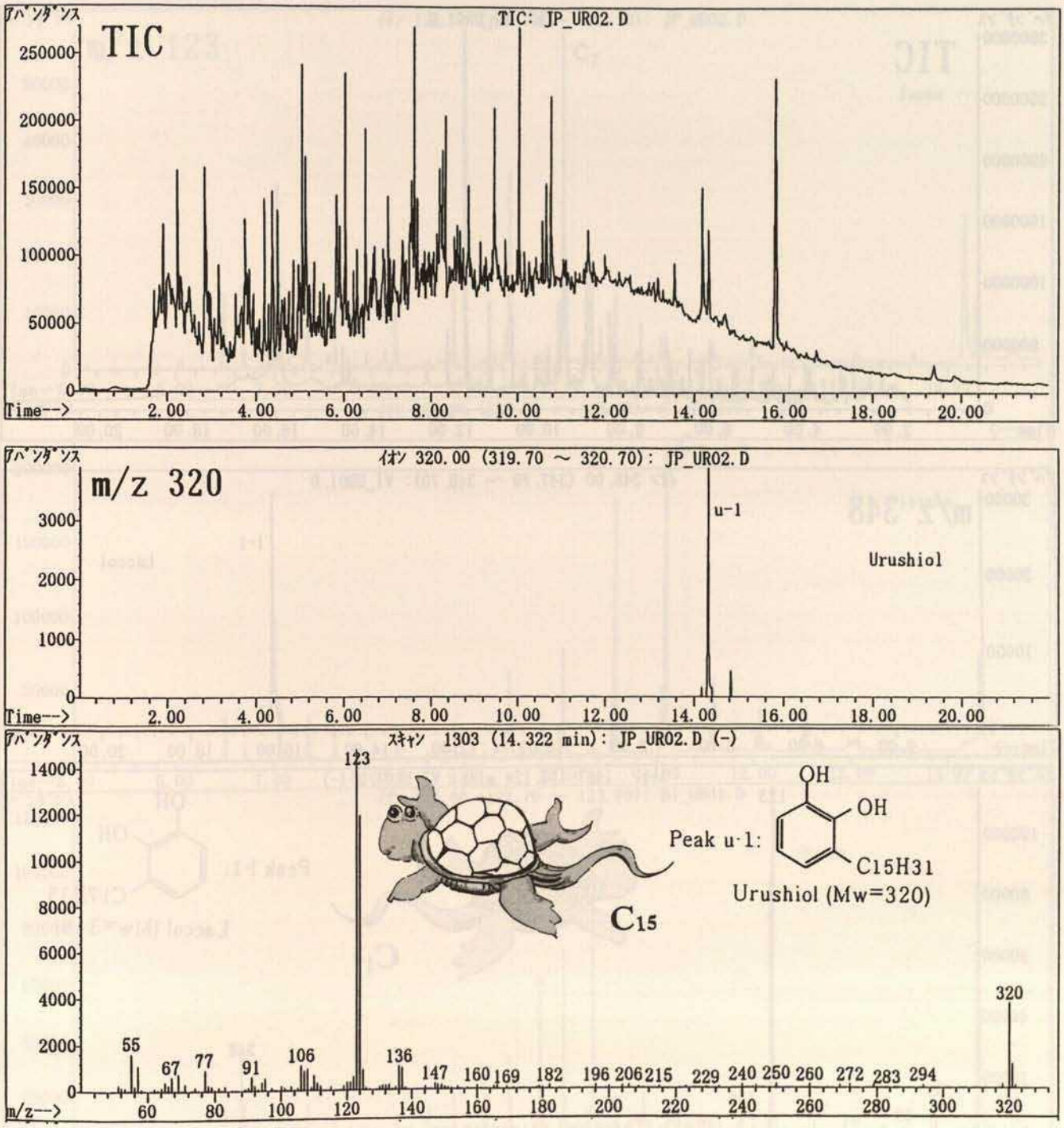



Fig. 5. Total ion chromatogram (TIC), mass (m/z 320) chromatogram and mass spectrum (urushiol) of *Rhus vernicifera* lacquer film

the relative intensity of 3-heptylcatechol (C7) is the highest in the *Rhus vernicifera* lacquer film, whereas in the *Rhus succedanea* lacquer film, that of 3-nonylcatechol (C9) is the highest.

It has been reported that at the α- and β-positions, the double bonds of the olefins are most susceptible to thermal cleavage. Therefore, as shown in figure 8, the highest yield of 3-heptylcatechol (C7) and 3-nonylcatechol (C9) can be attributed to the preferential cleavage at the α-position of the double bonds of the nucleus-14th and 16th chain C-O coupling for the urushiol and laccol polymers, respectively.

Alkylphenols were detected in the mass chromatograms (m/z 108) at 500 °C of the *Rhus vernicifera* and *Rhus succedanea* lacquer films as shown in figure 9. The alkylphenols that have the longest side chain are the pentadecylphenols in the *Rhus vernicifera* lacquer film and the heptadecylphenols in the *Rhus succedanea* lacquer film. These are believed to be the pyrolysis products of the nucleus-side chain C-O coupling in the urushiol and laccol polymers, respectively, because it has been inferred that dimerization of urushiol proceeds through the laccase-catalyzed nucleus-side chain C-O coupling, as well as C-C coupling. Furthermore, since the C-O coupling polymers should mainly

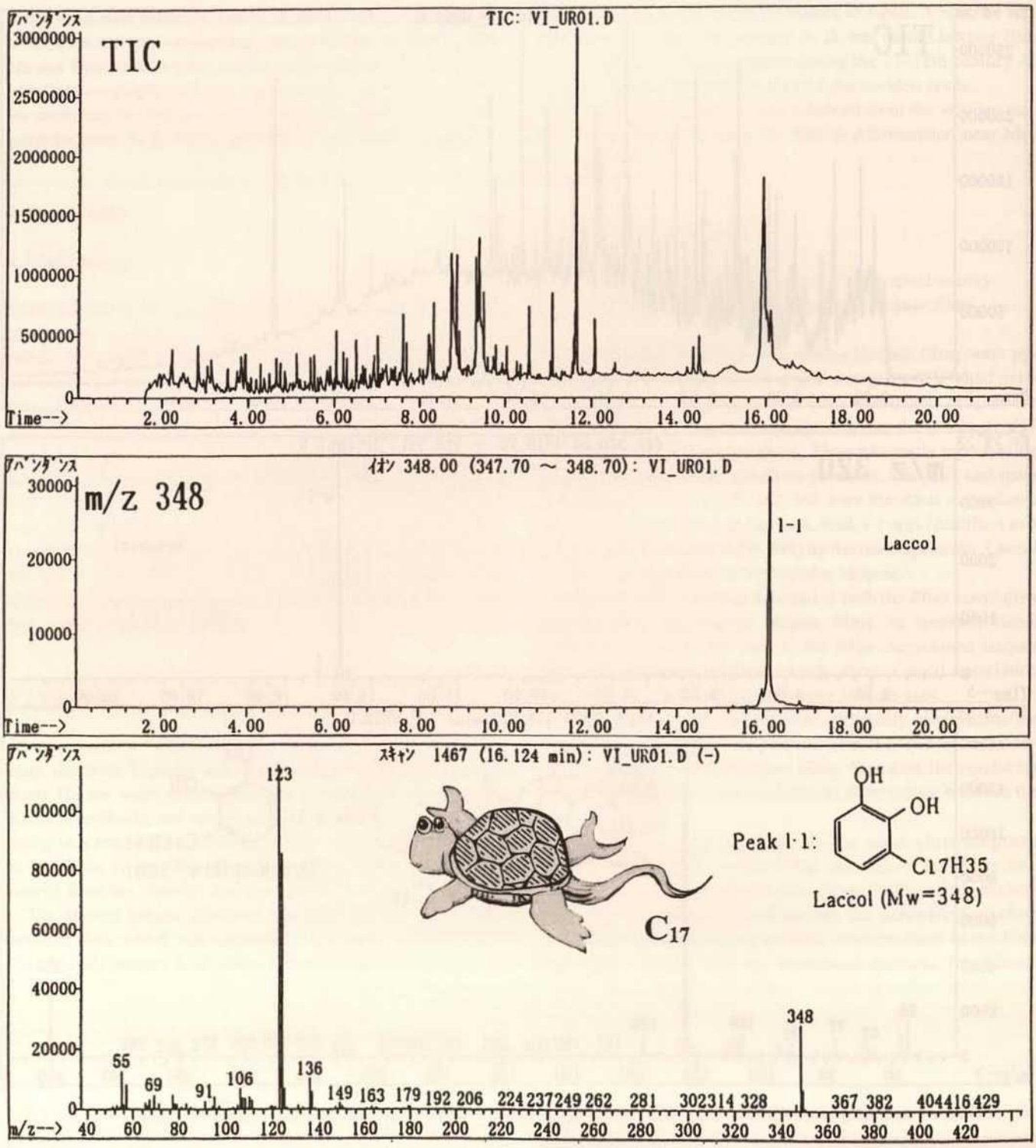



Fig. 6. TIC, mass (m/z 348) chromatogram and mass spectrum (laccol) of *Rhus succedanea* lacquer film

terminate with the alkyl- and monoalkenylcatechols, the pentadecylphenols and heptadecylphenols might be formed from such terminal groups, as shown in figure 8. Additionally, the relative intensity of the 2- and 3-heptylphenols (C7) is the highest in the *Rhus vernicifera* lacquer film, whereas in the *Rhus succedanea* lacquer film, that of the 2- and 3-nonylphenols (C9) is the highest. As shown in figure 9, the highest yield of the 2- and 3-heptylphenols (C7) and the 2- and 3-nonylphenols (C9) can be attributed to the preferential cleavage at the α-position of the double bonds of the nucleus-14th and 16th chain C-O coupling for the urushiol and laccol polymers, respectively.

Fragments such as the shorter side chain of alkylcatechols and alkylphenols were produced through release of the arm and removal of the long tail of the turtle at high temperatures. Furthermore, the relative intensity of the 2- and 3-heptylphenols (C7) is the highest in the *Rhus vernicifera* lacquer film, whereas in the *Rhus succedanea* lacquer film, that of the 2- and 3-nonylphenols (C 9) is the highest.

It is extremely important to determine whether objects that are claimed to be urushiware are actually created from urushi or some other resins. Urushiware can be precisely determined by the presence of urushiol or laccol with alkylcatechols and

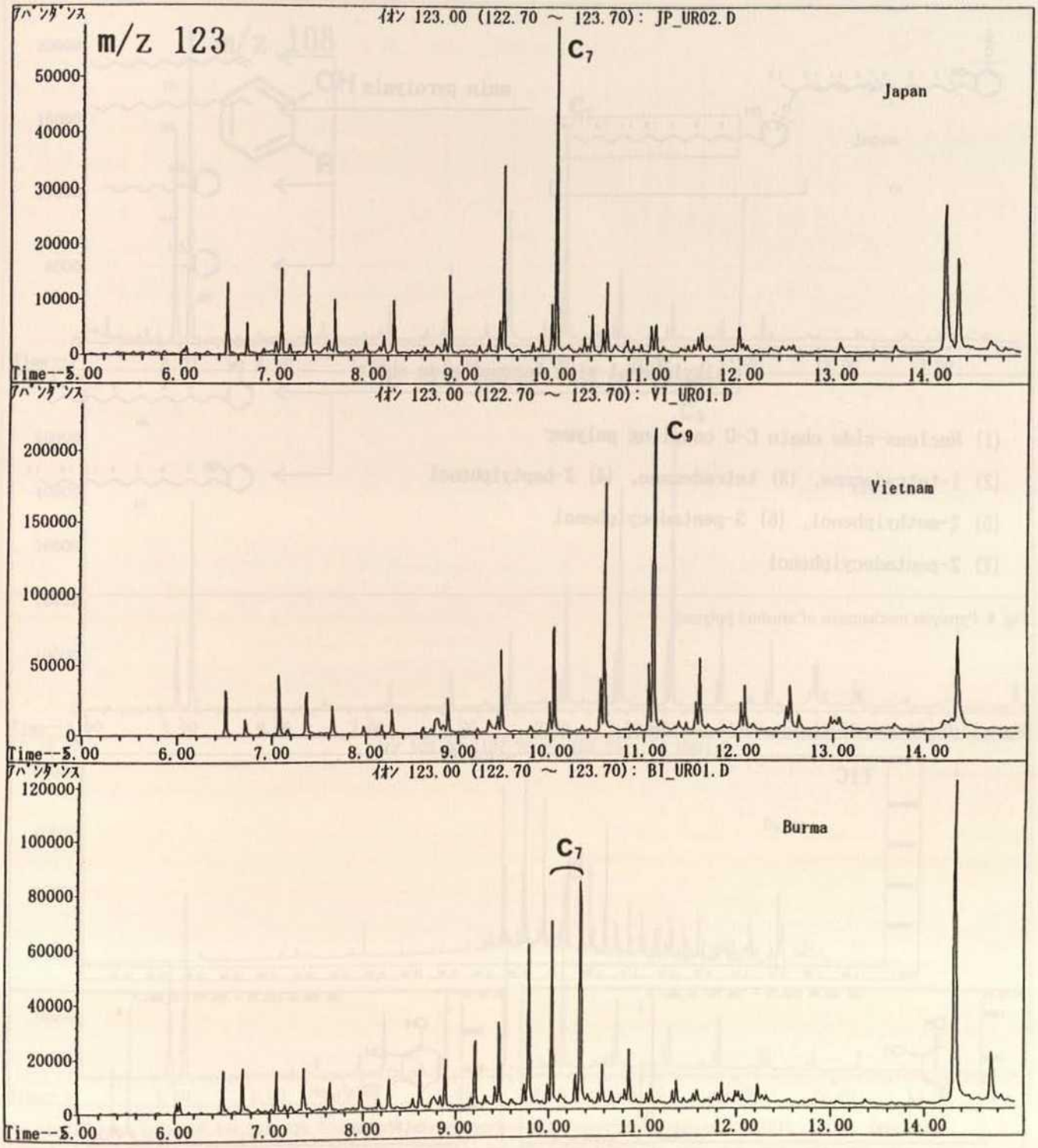



Fig. 7. Mass (m/z 123) chromatograms of lacquer films
Japan $C_7$ = 3-heptylcatechol; Vietnam $C_9$ = 3-nonylcatechol; Burma $C_7$ = 3- and 4-heptylcatechol

alkylphenols using pyrolysis-gas chromatography and mass spectrometry.

### *3.2 Pyrolysis-gas chromatography and mass spectrometry of* Melanorrhoea usitata *lacquer films*

*Melanorrhoea usitata* is a lacquer tree planted in Thailand and Burma. The sap of *Melanorrhoea usitata* is a latex composed of thitsiol, water, plant gum, glycoprotein and laccase enzyme. The *Melanorrhoea usitata* lacquer sap contains 3- and 4-heptadecadienylcatechols, as well as a series of ω-phenylalkylcatechols.

The *Melanorrhoea usitata* lacquer film was pyrolized at 500 °C. Figure 9 shows the TIC and the 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 being due to 4-heptadecenylcatechol (MW 346), 4-heptadecenylcatechol (MW 348), 3-(10-phenyldecyl)phenol (MW 310), 3-(10-phenyldecyl)catechol (MW 326), 4-(10-phenyldodecyl) phenol (MW 338) and 4-(12-phenyldodecyl)catechol (MW 354), respectively, based on the mass spectra. Since the C-O coupling

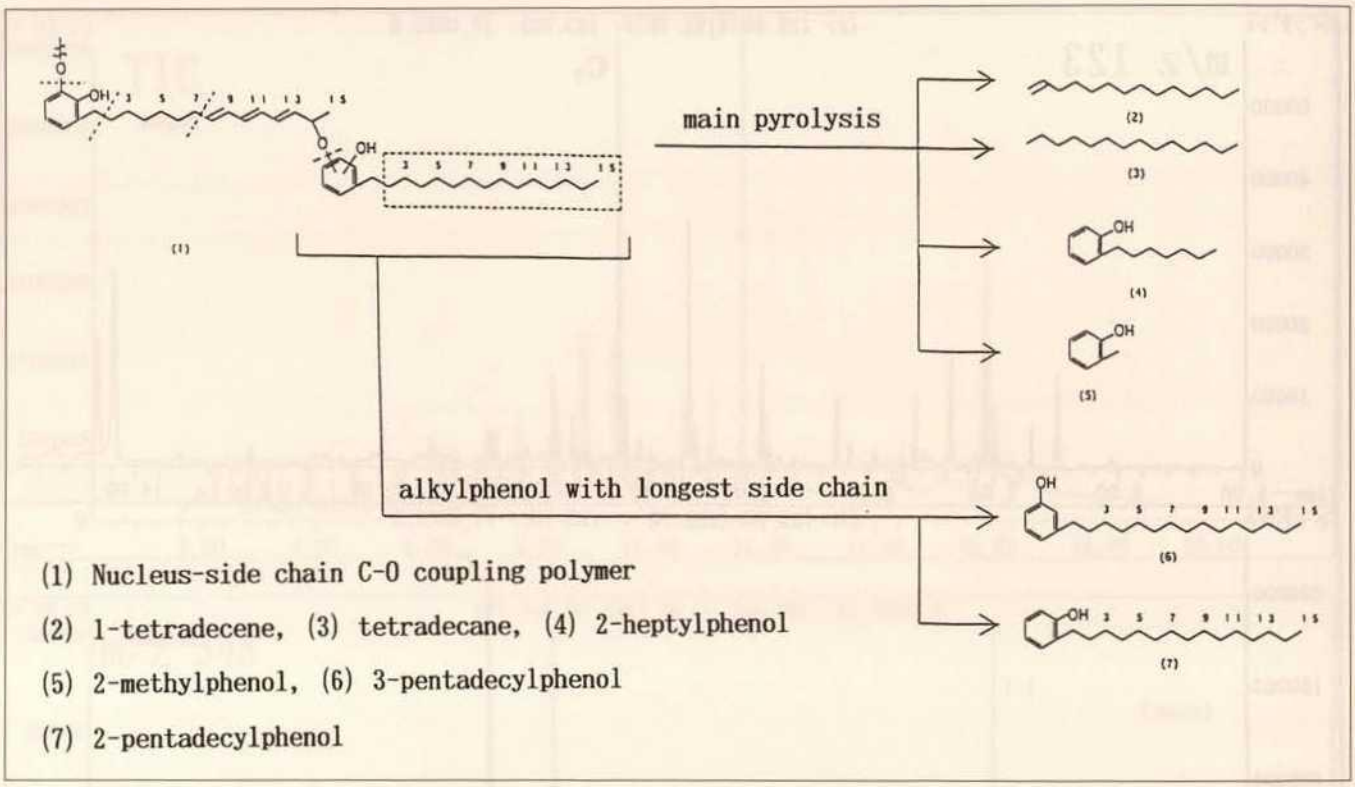
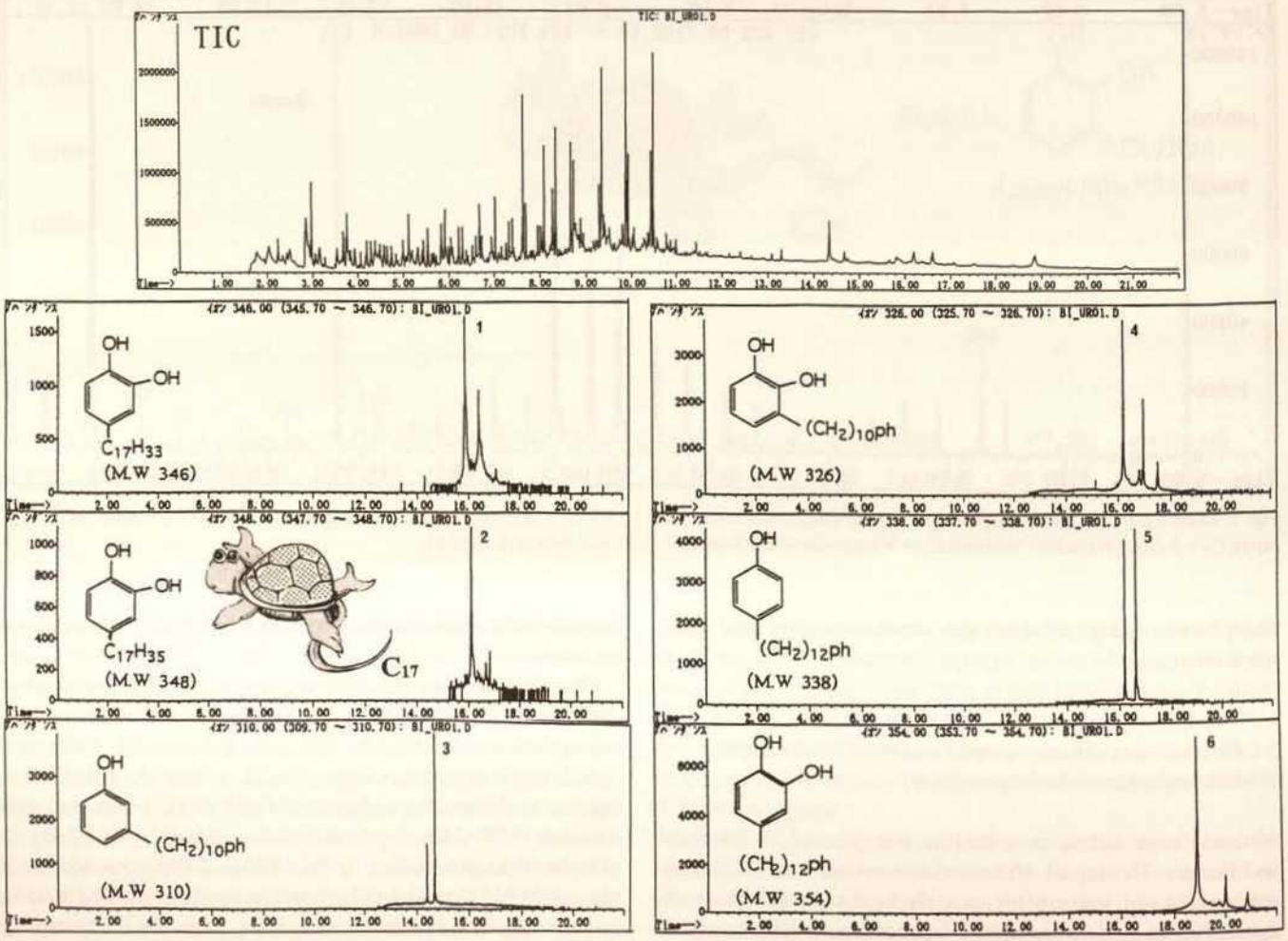



Fig. 8. Pyrolysis mechanisms of urushiol polymer

Fig. 9. Mass (m/z 108) chromatogram of lacquer films



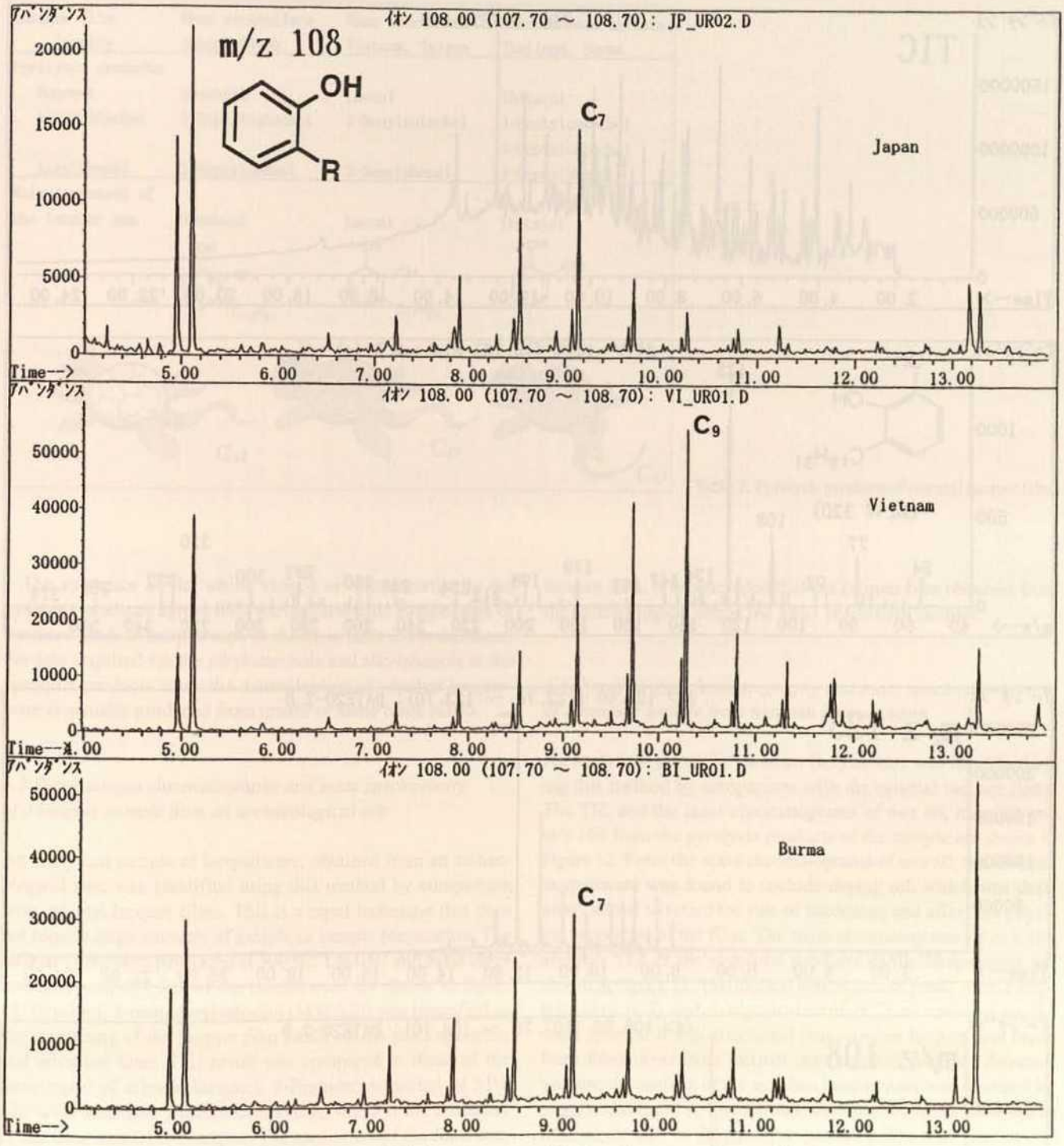



Fig. 10. TIC, mass (m/z 346, 348, 310, 326, 338 and 354) chromatograms of *Melanorrhoea usitata* lacquer film
Japan $C_7$ = 2-heptylphenol; Vietnam $C_9$ = 2-nonylphenol; Burma $C_7$ = 3- and 4-heptylphenol

polymers should be terminated with ω-phenylalkylcatechols, these compounds can be formed from such terminal groups. The molecular weight of laccol is 348, which is the weight of the dotted turtle with the long C 17 tail, that winds around one side.

As shown in figure 7, the peak pairs of the 3- and 4-alkylcatechols were detected in the mass chromatograms (m/z 123) at 500 °C of the *Melanorrhoea usitata* lacquer films. The relative intensity of the 3- and 4-heptylcatechols (C7) is the highest in the pyrolysis products of Burmese lacquer. The highest yield of the 3- and 4-heptylcatechols is thought to be mainly due to cleavage at the α-position of the double bonds of the nucleus-8th and 12th chain C-O coupling for the thitsiol polymers. The detected alkylphenols are likely to be the pyrolysis products of the nucleus-side chain C-O coupling the thitsiol polymers. The dimerization of the lacquer monomers is thought to proceed through the laccase-catalyzed nucleus-side chain C-O coupling as well as the C-C coupling. The yields of the 2- and 3-heptylphenols (C7) are the highest as shown in figure 10. The α- and β-positions of the double bonds of the olefin are susceptible to thermal cleavage so that these highest yields are thought to be primarily produced due to cleavage at the α-position of the double bonds of thitsiol such as the 3- and 4-(heptadeca-8,11-dienyl)catechols.

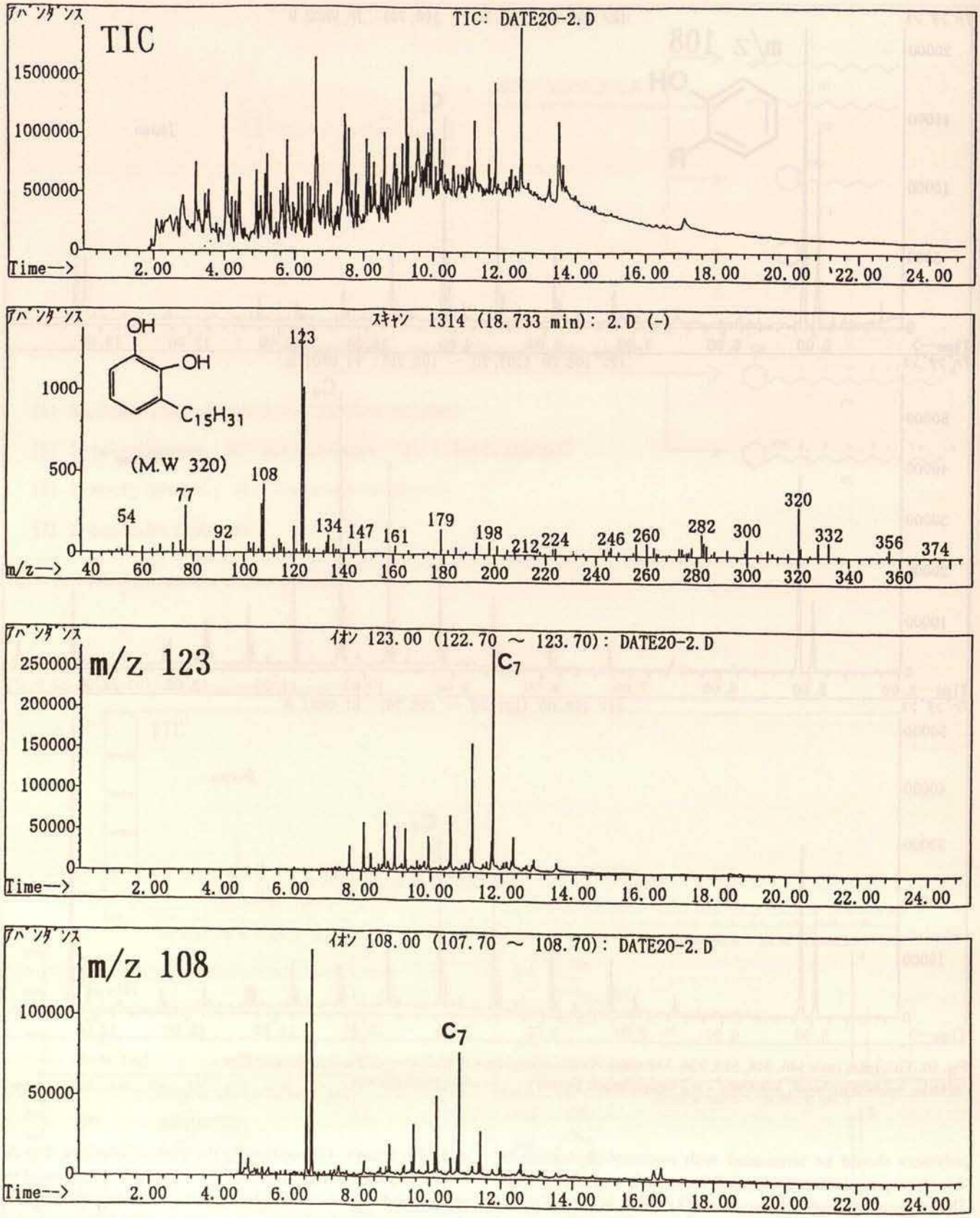



Fig. 11. The pyrolysis data of an archaeological lacquer film excavated from Meiji University campus in Tokyo, Japan

| Lacquer film<br>Country | Rhus vernicifera<br>Japan, China | Rhus succedanea<br>Vietnam, Taiwan | Melanorrhoea usitata<br>Thailand, Burma |
|---|---|---|---|
| Pyrolysis products | | | |
| Monomer | Urushiol | Laccol | Thitsiol |
| Alkylcatechol | 3-Heptylcatechol | 3-Nonylcatechol | 3-Heptylcatechol<br>4-Heptylcatechol |
| Alkylphenol | 3-Heptylphenol | 3-Nonylphenol | 3-Heptylphenol |
| Main component of the lacquer sap | Urushiol | Laccol | Thitsiol |

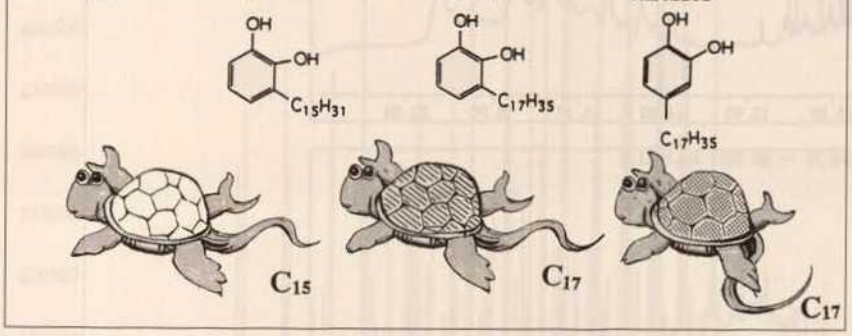






Table 2. Pyrolysis products of oriental lacquer films

The existence of the white, striped or dotted turtles in the pyrolysis products agrees with the characteristic components of the three kinds of lacquer saps as shown in table 2. Furthermore, the data acquired for the alkylcatechols and alkylphenols in the pyrolysis products allow the determination of whether lacquerware is actually produced from urushi or some other resins.

### *3.3 Pyrolysis-gas chromatography and mass spectrometry of a lacquer sample from an archaeological site*

An analytical sample of lacquerware, obtained from an archaeological site, was identified using this method by comparison with oriental lacquer films. This is a rapid technique that does not require large amounts of sample or sample preparation. The lacquer films were pyrolyzed at 500 °C. The TIC and mass chromatograms of m/z 320 of the lacquerware are shown in figure 11. Urushiol, 3-pentadecylcatechol (MW 320) was identified as the monomers 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-heptadecylcatechol of MW 348. This was not detected in the ancient lacquer film, except for 3-pentadecylcatechol of MW 320. The monomers of the *Melanorrhoea usitata* lacquer are thitsiol components with saturated and monoenyl side chains such as 4-heptadecylcatechol (MW 348) and 3- and 4-(ω-phenylalkyl)phenols and catechols. These components, except for 3-pentadecylcatechol of MW 320, were not detected in the ancient lacquer film.

In the TIC and mass chromatograms (m/z 108) of the *Rhus succedanea* lacquer film, alkylphenols were also detected in the old lacquer film. However, two differences were found. The longest side chain of the alkylphenols is C 17, and the relative peak intensity of 2-nonylphenol (C9) is the highest in this film. The TIC and mass chromatograms (m/z 108) of *Melanorrhoea usitata* are different from those of the old lacquer film, because phenylalkylphenols are detected in this film, but not in the old lacquer film. It is concluded that the lacquer film obtained from the archaeological site is the *Rhus vernicifera* lacquer.

### *3.4 Pyrolysis-gas chromatography and mass spectrometry of a lacquer sample from* namban *lacquerware*

An analytical sample of *namban* lacquerware was identified using this method by comparison with the oriental lacquer films. The TIC and the mass chromatograms of m/z 60, m/z 123 and m/z 108 from the pyrolysis products of the sample are shown in figure 12. From the mass chromatograms of m/z 60, the *namban* lacquerware was found to include drying oil, which was definitely added to retard the rate of hardening and affect 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 shown in figure 12. The highest abundance of peaks were 2-heptylphenol (C7) and 3-heptylcatechol (C7) as revealed by the mass spectra. It was concluded that *namban* lacquer was made from *Rhus vernicifera* lacquer sap. Urushiol was not detected, because the surface of the *namban* lacquerware was oxidized by oxygen and light. A type of wax was detected in the mass spectrum of the TIC of the pyrolysis products. The wax was used to polish the surface of the lacquerware.

### *3.5 Pyrolysis-gas chromatography and mass spectrometry of an analytical sample of old lacquerware exported from Asia*

An analytical sample of the lacquerware exported from Asia was analyzed using pyrolysis-gas chromatography and mass spectrometry at 500 °C. The lacquerware was identified by comparison with the oriental lacquer films. The TIC and mass chromatograms of m/z 123 and m/z 108 for the pyrolysis products of the sample are shown in figure 13. Alkylcatechols and alkylphenols were detected in the mass chromatograms. The higher abundance of peaks by comparison with nonylcatechols and nonylphenol were the 3- and 4-heptylcatechols (C7) and 2-heptylphenol (C7) as determined by mass spectra. It is concluded

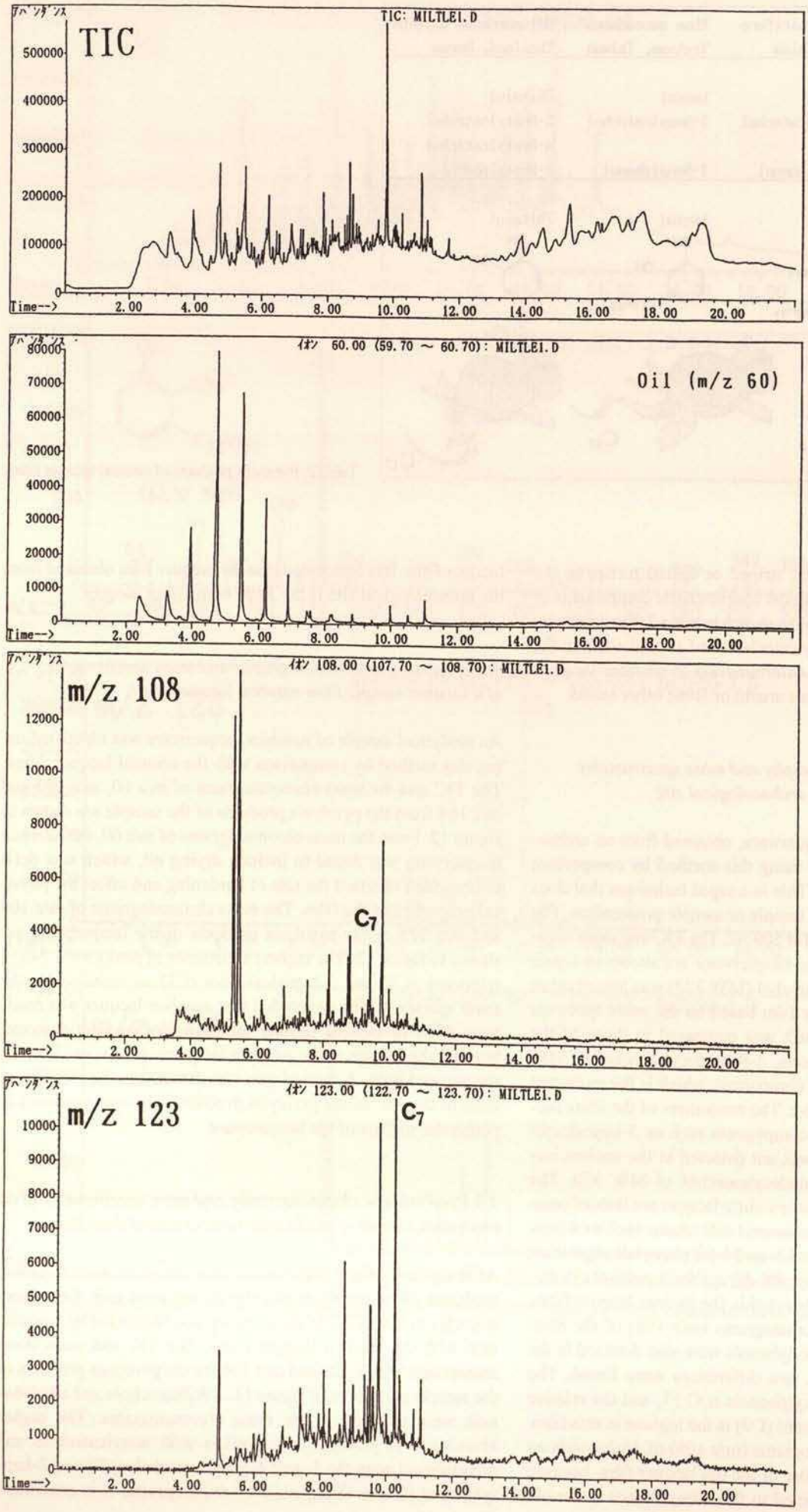



Fig. 12. The pyrolysis data of the *namban* lacquer film

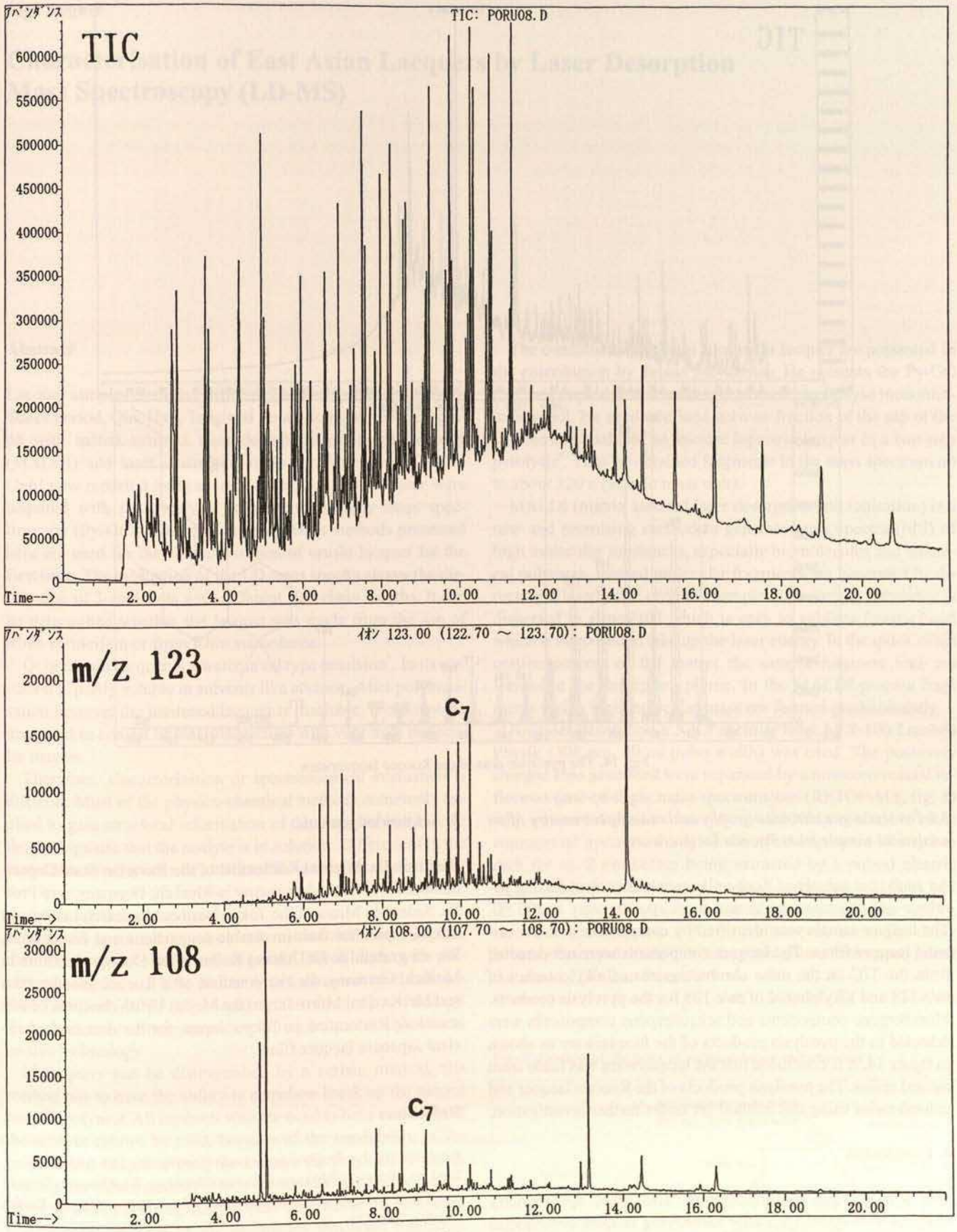



Fig. 13. The pyrolysis data of an old lacquerware exported from Asia

that the lacquerware was produced using *Melanorrhoea usitata* lacquer sap. Thitsiol was not detected from the pyrolysis data, because the surface of lacquerware was oxidized by oxygen and the effect of 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 bees wax, as revealed by the mass spectra. The bees wax was used to protect and polish the surface of lacquerware.

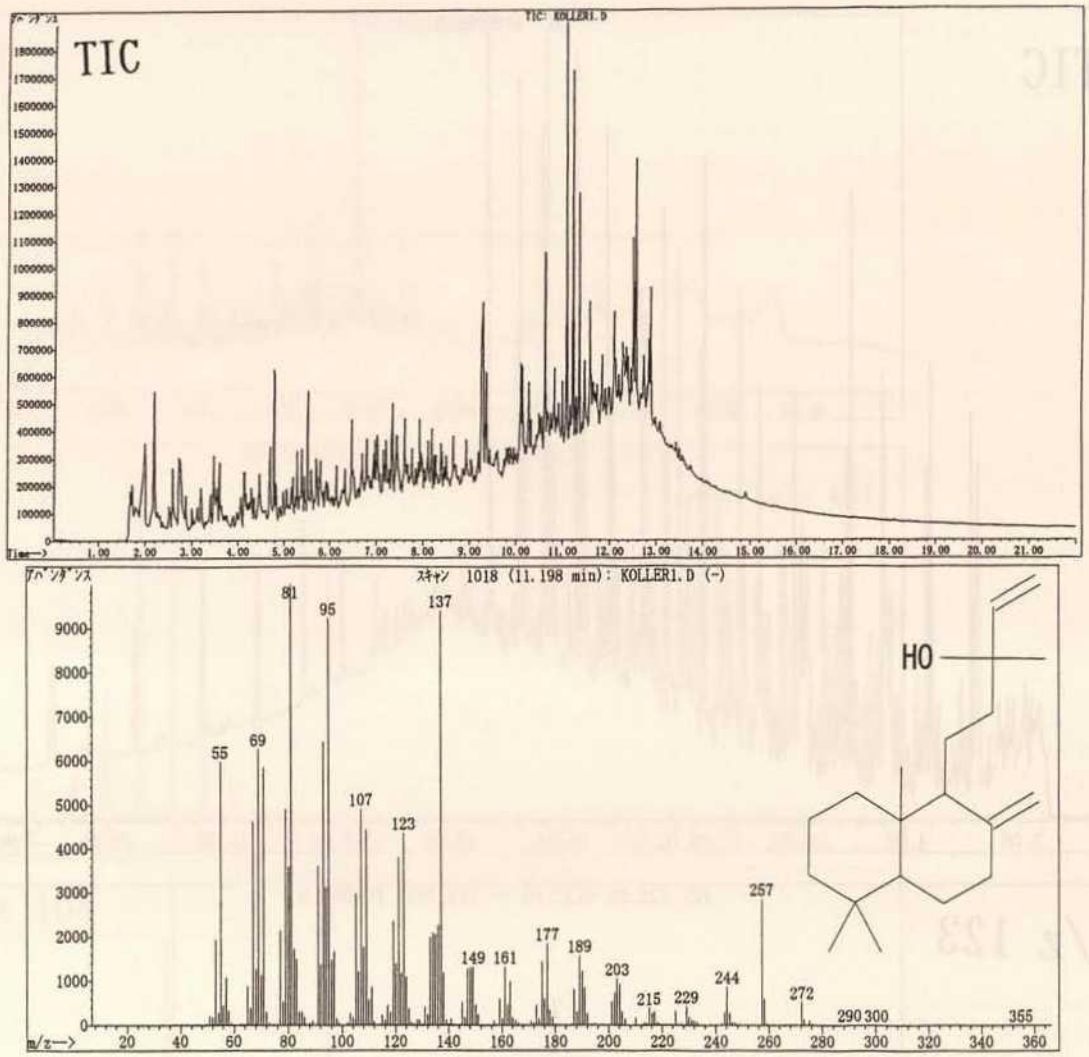



Fig. 14. The pyrolysis data of the Rococo lacquerware

*3.6 Pyrolysis-gas chromatography and mass spectrometry of an analytical sample from Rococo lacquerware*

An analytical sample of Rococo lacquer was analyzed using pyrolysis-gas chromatography and mass spectrometry at 500 °C. The lacquer sample was identified by comparison with the oriental lacquer films. The lacquer components were not detected from the TIC on the mass chromatograms of alkylcatechol of m/z 123 and alkylphenol of m/z 108 for the pyrolysis products. Monoterpene components and sesquiterpene components were detected in the pyrolysis products of the lacquerware as shown in figure 14. It is concluded that the lacquerware was made from natural resins. The pyrolysis products of the Rococo lacquer and natural resins using this method are under further investigation.

## 4. Conclusion

The pyrolysis-gas chromatography and mass spectrometry analysis is effective for easily identifying lacquer components and the origin of different types of lacquers. Furthermore, this method can be used for discriminating between lacquer and other resins for the conservation or restoration of lacquerware.

## Photo Credits

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## 5. Acknowledgements

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