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Determination of the type of lacquer on East Asian lacquer ware

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ABSTRACT

Simple and easy analytical methods, which are applicable to precious artistic objects, have long been desired to determine the type of lacquer on lacquer ware. Direct inlet mass spectrometry (DIMS) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) were applied to the determination of the coating film on a lacquered wooden dish obtained in Okinawa. The above two-step mass spectrometry confirmed the coating film: the lacquer to be East Asian lacquer, or natural urushi derived from *Rhus verniciflua*. These two-step analyses are very useful for the determination of the type of lacquer on any lacquer ware. The first step analysis with DIMS is used to distinguish the natural urushi including the urushi-type lacquers from non-natural urushi: imitation urushi and lacquer containing synthetic resins. And the second step with Py-GC/MS is used to discriminate one type among the three natural urushi-type lacquers. These two-step analyses need only a small amount of sample ranging 0.01–0.5 mg without any pre-treatment so that these analyses can be used for precious lacquer ware with archeological interest.

1. Introduction

A technical art of making lacquer ware has a very long history in East Asia [1–3]. Its essential part is the use of urushi: East Asian lacquer, the world oldest one, as a coating material. Because urushi gives excellent toughness and brilliance to lacquer ware for a long period of time, it has been highly appreciated as a coating material on traditional artistic handicrafts [4].

The lacquer ware together with other East Asian objects of art was taken to Europe in considerable quantity during the 16th century [5]. Since then, it became so fashionable that European craftsmen undertook to make their own. Because the habitat of the varnish tree from which urushi is derived is limited only in East Asia, they were forced for their lacquer ware to use imitation urushi.

In the 20th century, various kinds of synthetic resins were developed and introduced as coating materials. They have been used as lacquer on objects ranging from artistic handicrafts to popular products in large quantities. Quite recently, artificial urushi has successfully been synthesized for the replacement of natural urushi [6]. Broadly speaking, there exist, at present, three types of lacquer excluding the synthetic urushi; they are natural urushi including natural urushi-type lacquer, imitation urushi and lacquer containing synthetic resins. By the way, there are known to be three types of varnish trees from which the natural urushi-type lacquer is derived. They are *Rhus verniciflua*, *Rhus succedanea* and *Melanorrhoea usitate*. Each habitat of these three trees is different from those of the others: the habitat of the first type: *R. verniciflua* is China, Japan and Korea, and that of the second is North Vietnam and Taiwan whereas that of the third is Thai and Myanmar. Furthermore, the principal ingredients of the sap derived from these trees are also different and are called urushiol, laccol and thitsiol, respectively. The identification of the natural urushi-type lacquer, therefore, gives us information about the place where the lacquer was produced.

From the archeological point of view, coating films on lacquer ware have been investigated with modern analytical techniques such as solid-state carbon-13 nuclear magnetic resonance spectroscopy [7], Fourier transform infrared spectroscopy [8] and X-ray photoelectron spectroscopy [9–12]. These methods revealed useful information about the structure and chemical state of these films. However, they did not unfortunately give any direct information about the type of coating material. The analytical method is, therefore, desirable to identify the type of coating material on lacquer ware.

In this paper, direct inlet mass spectrometry (DIMS) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) were successfully applied to the identification of the coating film on a lacquered wooden dish.

2. Experimental

2.1. Sample

A small amount of sample was scraped off from a lacquered wooden dish shown in Fig. 1. The dish was purchased at an antique store on Okinawa prefecture in Japan. Okinawa is famous for “Ryukyushikki”, or “Ryukyu lacquer ware”. Okinawa Island was

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Fig. 1. The lacquered wooden dish, where coated lacquer was analyzed.

ruled by Ryukyu kingdom from the 15th century to the 19th century. Ryukyushikki has been produced since Ryukyu kingdom period [13].

As references, we prepared one synthesized 3-pentadecylcatechol [14] and three types of lacquer films. The former is a typical component of lacquer, whereas the latter three films were prepared in the following way from the genuine sap of three types of lacquer trees: *R. verniciflua*, *R. succedanea* and *M. usitate*. The main components of *R. verniciflua*, *R. succedanea* and *M. usitate* lacquer are urushiol, laccol and thitsiol, respectively. The composition of urushiol, laccol and thitsiol is shown in Tables 1–3 [15]. Each sap was treated with the traditional mixing processes called Kurome and Nayashi [3], then coated on a glass plate followed by laccase-catalyzed oxidative coupling [16] in a humidity-controlled chamber with a relative humidity of 70–90% at 20 °C for 7 days. Thus produced lacquer film was removed from the chamber and stored open space.

Table 1
Composition of urushiol.

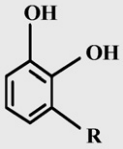
	R	*Mr*	%
	8(Z),11(E),13(Z)-$C_7H_{14}CH{=}CHCH_2CH{=}CHCH{=}CHCH_3$	314	55.4
	8(Z),11(E),14-$C_7H_{14}CH{=}CHCH_2CH{=}CHCH_2CH{=}CH_2$	314	7.4
	8(Z),11(E),13(E)-$C_7H_{14}CH{=}CHCH_2CH{=}CHCH{=}CHCH_3$	314	1.7
	8(Z),11(Z)-$C_7H_{14}CH{=}CHCH_2CH{=}CHC_3H_7$	316	6.5
	8(Z),11(E)-$C_7H_{14}CH{=}CHCH_2CH{=}CHC_3H_7$	316	4.4
	8(Z)-$C_7H_{14}CH{=}CHC_6H_{13}$	318	15.0
	10(Z)-$C_9H_{18}CH{=}CHC_4H_9$	318	1.5
	$C_{15}H_{31}$	320	4.5
	8(Z),11(Z)-$C_7H_{14}CH{=}CHCH_2CH{=}CHC_5H_{11}$	344	1.8
	10(Z)-$C_9H_{18}CH{=}CHC_6H_{13}$	346	1.5

Table 2
Composition of laccol.

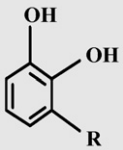
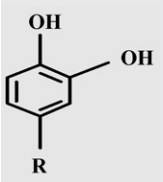
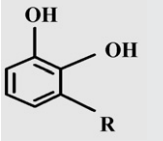
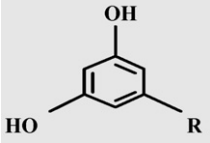
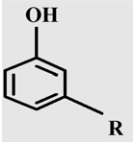
	R	*Mr*	%
	$C_{15}H_{31}$	320	1.3
	10(Z),13(E),15(E)-$C_9H_{18}CH{=}CHCH_2CH{=}CHCH{=}CHCH_3$	342	15.6
	8(Z),11(Z)-$C_7H_{14}CH{=}CHCH_2CH{=}CHC_5H_{11}$	344	4.9
	10(Z),13(E)-$C_9H_{18}CH{=}CHCH_2CH{=}CHC_3H_7$	344	1.7
	10(Z)-$C_9H_{18}CH{=}CHC_6H_{13}$	346	17.2
	12(Z)-$C_{11}H_{22}CH{=}CHC_4H_9$	346	2.4
	8(Z)-$C_7H_{14}CH{=}CHC_8H_{17}$	346	1.9
	$C_{17}H_{35}$	348	1.8

Table 3
Composition of thitsiol.

	R	*Mr*	%
	$C_{15}H_{29}$(cis)	318	
	$C_{15}H_{31}$	320	0.7
	$(CH_2)_{10}C_6H_5$	326	0.7
	$C_{17}H_{29}$(all cis)	342	1.1
	$C_{17}H_{31}$(all cis)	344	20.5
	$C_{17}H_{33}$(trans)	346	
	$(CH_2)_{12}C_6H_5$	354	3.6
	$C_{15}H_{29}$(cis)	318	
	$C_{15}H_{31}$	320	3.9
	$(CH_2)_{10}C_6H_5$	326	7.5
	$C_{17}H_{29}$(all cis)	342	
	$C_{17}H_{31}$(all cis)	344	19.7
	$C_{17}H_{33}$(cis)	346	
	$C_{17}H_{33}$(trans)	346	
	$(CH_2)_{12}C_6H_5$	354	36.0
	$(CH_2)_{10}C_6H_5$	326	0.7
	$(CH_2)_{12}C_6H_5$	354	2.1
	$(CH_2)_{10}C_6H_5$	310	1.4
	$C_{17}H_{31}$	328	
	$(CH_2)_{12}C_6H_5$	338	
	$CH_2CO(CH_2)_{10}C_6H_5$	352	0.4
	$CH_2CH(OH)C_{17}H_{29}$	370	
	$CH_2CH(OH)C_{17}H_{31}$	372	
	$CH_2CO(CH_2)_{12}C_6H_5$	380	
	$(CH_2)CH(OH)(CH_2)_{12}C_6H_5$	382	

2.2. DIMS condition

Direct inlet mass spectrometry was performed with a double-focusing mass spectrometer: JMS-GCmate (JEOL Inc.). The sample (0.01 mg) was placed into a glass tube. The tube was set on an inlet-probe. The tube set on the inlet-probe was introduced into the chamber of the mass spectrometer, and then the tube was heated at 400 °C simultaneously with starting electron ionization. The ionization energy was 70 eV. Magnetic field scan and linked scan at constant B^2/E mass spectra, where B and E are magnetic and electric sector field strength, respectively, were recorded under this condition.

2.3. Py-GC/MS condition

pyrolysis-gas chromatography/mass spectrometry was carried out with a vertical microfurnace-type pyrolyzer: PY-2010D (Fron-

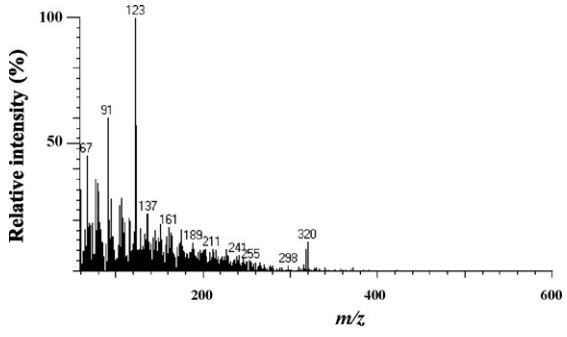


Fig. 2. Magnetic field scan mass spectrum of the sample shown in Fig. 1.

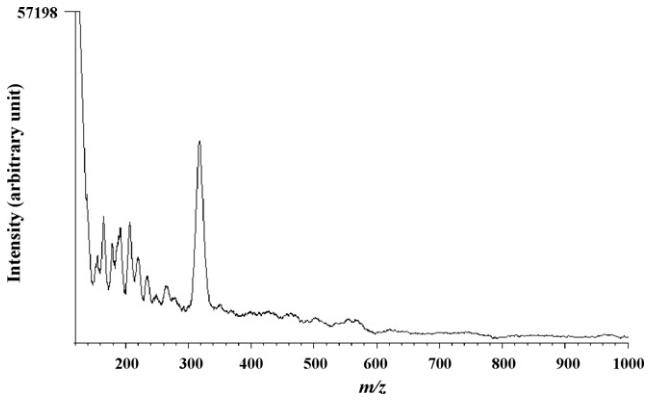


Fig. 3. Linked scan at constant B^2/E of m/z 123 mass spectrum of the sample shown in Fig. 1.

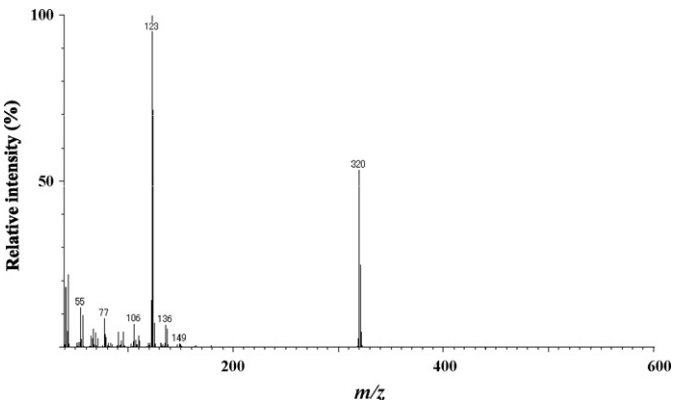


Fig. 4. Magnetic field scan mass spectrum of synthesized 3-pentadecylcatechol.

tier Lab.), a gas chromatograph: Agilent 6890 (Agilent Ltd.) and a mass spectrometer: JMS-Q1000GC (JEOL Ltd.). A sample film of 0.5 mg was placed in a platinum sample cup, which was set at the top of the pyrolyzer kept at room temperature. The sample cup was inserted into a furnace at 400 °C, followed by heating a gas chromatograph oven, which was programmed to raise the temperature at a constant rate of 20 °C/min in a range from 40 °C to 330 °C. Helium was used as a carrier gas at a flow rate of 10 ml/min in the pyrolyzer, which was reduced to 1 ml/min with a splitter at the capillary column in the gas chromatograph. A stainless steel capillary column with an inner diameter of 0.25 mm and a length of 30 m coated with 0.25 μm thick Ultra Alloy PY-2 (Frontier Lab.)—dimethylpolysiloxane 100%—was used for separation. Scanning mass spectra were recorded using electron ionization with an ionization energy of 70 eV.

3. Results and discussion

3.1. DIMS

The magnetic field scan mass spectrum of the sample is shown in Fig. 2. The spectrum was complicated, because the fragment ions were attributed to a number of thermal degradation products. A linked scan at constant B^2/E of m/z 123, where the base peak was

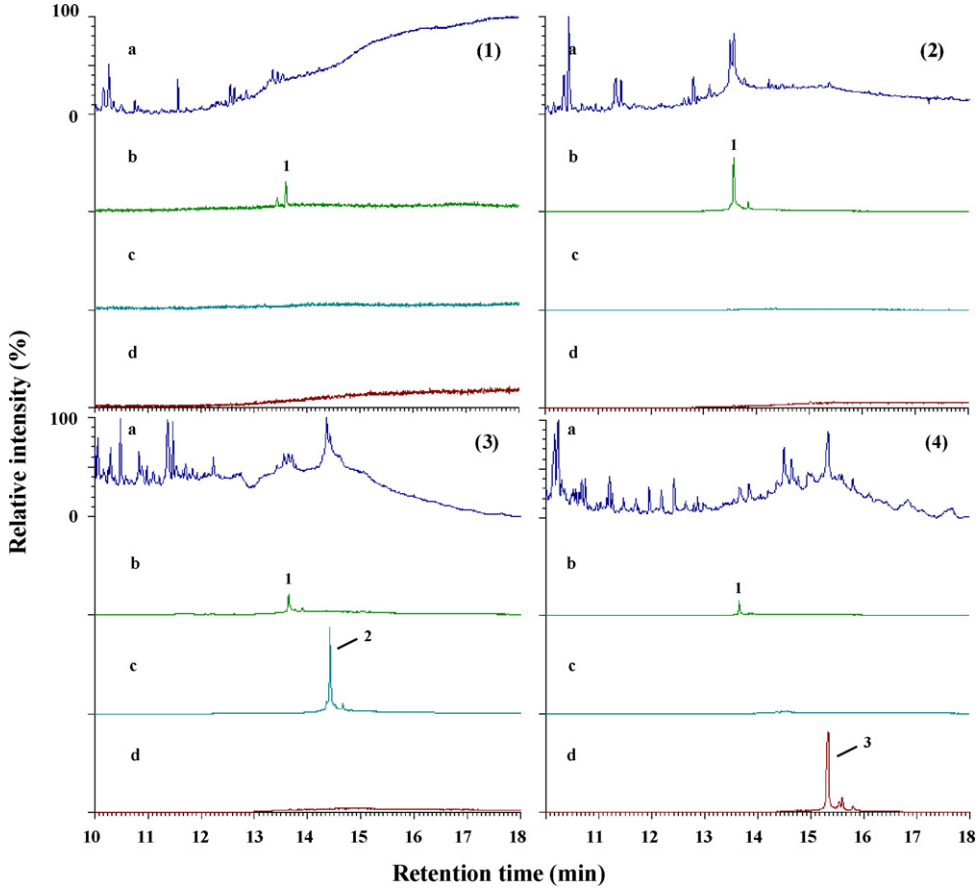


Fig. 5. TIC and mass chromatograms (m/z 320, 348, 354) of (1) the sample shown in Fig. 1, the lacquer films of (2) *Rhus verniciflua*, (3) *Rhus succedanea* and (4) *Melanorrhoea usitate*. a: TIC, b: mass chromatogram (m/z 320), Peak 1: 3-pentadecylcatechol, c: mass chromatogram (m/z 348), Peak 2: 3-heptadecylcatechol, d: mass chromatogram (m/z 354), Peak 3: 3-(12-phenyldodecyl)catechol.

observed, was performed to investigate the precursor ion. The spectrum is shown in Fig. 3. The precursor ion was detected at around m/z 320. The relative molecular mass of 3-pentadecylcatechol, which is the component of urushiol, laccol and thitsiol, is 320. The synthesized 3-pentadecylcatechol was analyzed with DIMS and the magnetic field scan mass spectrum shown in Fig. 4 was obtained. The molecular ion and the base ion peak were observed at m/z 320 and m/z 123, respectively. The fragment ion at m/z 123 is attributed to the preferential cleavage of the side chain at the β-position to the aromatic ring. Comparing this spectrum and the linked scan mass spectrum of the sample, it is concluded that the precursor ion observed at around m/z 320 is ascribed to 3-pentadecylcatechol, which is thermal degradation products of the sample. Natural urushi was reported to be hardened by laccase-catalyzed oxidative coupling of urushiol, laccol and thitsiol [15] and autoxidative cross-linkage of these side chains [17–19]. In these reactions, saturated side chains compose terminal functions of the polymer, because unsaturated side chains are active but saturated side chains are not, so unsaturated components like alkenylcatechols compose polymer skeleton. Therefore, 3-pentadecylcatechol is preferentially separated out by the thermal degradation from the terminal groups at the lower temperature like 400 °C than 500 °C, at which the East Asian lacquer film is completely pyrolyzed [20].

Thus it is revealed that the sample is a natural urushi, because 3-pentadecylcatechol is its typical component.

3.2. Py-GC/MS

The sample and the three reference lacquer films were analyzed with the pyrolysis-gas chromatography/mass spectrometry. A total ion chromatogram (TIC) and three mass chromatograms at m/z 320, 348 and 354 of the sample, and the corresponding chromatograms of the three reference lacquer films are shown in Fig. 5.

The comparison of the three Figs. 2–4, strongly suggests the possibility of the identification to a specific lacquer film among the three types. The TICs were rather complicated so that the TIC alone could not be used for the identification. The longest retention time, beyond which reasonably strong peaks were no longer observed, was, however, different among the three TICs: no strong peaks were observed beyond 14, 15 and 16 min in (2)-a, (3)-a and (4)-a, respectively. Patterns of three mass chromatograms at m/z 320, 348 and 354 were quite different among the three Figs. 2–4, and could be used for the identification. In all mass chromatograms at m/z 320, a similar peak was observed at the retention time of 13.62, 13.63 and 13.65 in (2)-b, (3)-b and (4)-b, respectively. These peaks (designated as peak 1) were all assigned to 3-pentadecylcatechol by mass spectra. The mass spectrum of the sample was shown in Fig. 6-(1). A molecular ion peak and a base ion peak were detected at m/z 320 and 123, respectively. In mass chromatograms at m/z 348, no peak was observed in Fig. 5-(2)-c and (4)-c, whereas a strong peak (designated as peak 2) was observed at the retention time of 14.42 min in (3)-c. The peak was assigned to 3-heptadecylcatechol by mass spectrum shown in Fig. 6-(2). A molecular ion peak and a base ion peak were detected at m/z 348 and 123, respectively. In mass chromatograms at m/z 354, no peak was observed in Fig. 5-(2)-d and (3)-d, whereas a strong peak (designated as peak 3) was observed at the retention time of 15.30 min in (4)-d. The peak was assigned to 3-(12-phenyldodecyl)catechol by a mass spectrum shown in Fig. 6-(3). A molecular ion peak and a base ion peak were detected at m/z 354 and 123, respectively. It should be noted that the intensity of the peak 2 and 3 was substantially larger than that of the peak 1 in Fig. 5-(3) and (4), respectively.

These characteristic patterns of the chromatograms of the three reference lacquer films could well be explained by the compositions of urushiol, laccol and thitsiol, which are shown in Tables 1–3,

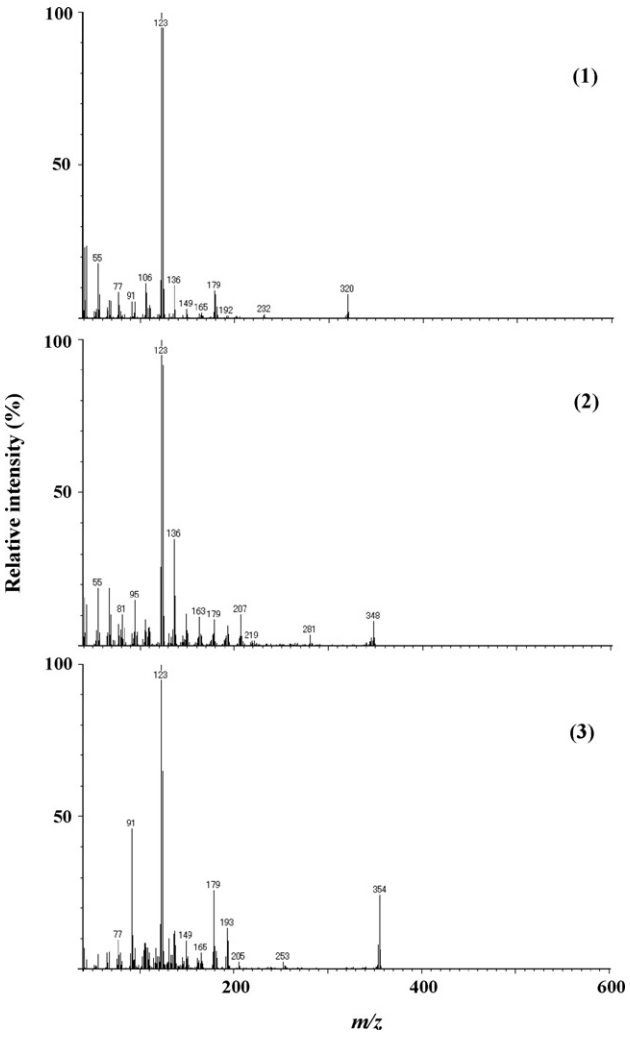


Fig. 6. Mass spectra of the peaks 1, 2 and 3. (1) 3-pentadecylcatechol, (2) 3-heptadecylcatechol, and (3) 3-(12-phenyldodecyl)catechol.

respectively. 3-pentadecylcatechol observed in all the three chromatograms is one of the typical pyrolysis products of urushiol, laccol and thitsiol polymers [17–19]. And 3-heptadecylcatechol and 3-(12-phenyldodecyl)catechol are a typical pyrolysis product of laccol and thitsiol polymers, respectively[17–19].

The pattern of the chromatograms of the sample shown in Fig. 5-(1) agreed well with that of those of the reference film shown in (2). No substantial peaks were observed beyond the retention time of 14 min in TIC as shown in (1)-a. No peak was observed in the two mass chromatograms at m/z 348 and 354, as shown in (1)-c and (1)-d. The peak 1 was observed at the retention time of 13.63 min in the mass chromatogram at m/z 320, as shown in (1)-b. This peak was assigned to 3-pentadecylcatechol by a mass spectrum in which molecular ion peak was detected at m/z 320. The base peak of the mass spectrum was, furthermore, observed at m/z 123. The present agreement leads to the conclusion that the sample is well identified as the lacquer made neither from *R. succedanea* nor from *M. usitate*, but from *R. verniciflua*.

4. Conclusions

The coating film on a lacquered wooden dish obtained in Okinawa was analyzed with direct inlet mass spectrometry (DIMS) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). These two-step analyses are useful for the determination

of the type of lacquer on any lacquer ware. The first step analysis with DIMS is used to distinguish the natural urushi including the urushi-type lacquers from non-natural urushi: imitation urushi and lacquer containing synthetic resins. And the second step with Py-GC/MS is used to discriminate one type among the three natural urushi-type lacquers.

The coating film was confirmed to be natural urushi derived from *R. verniciflua*. Ryukyu Kingdom imported the sap of *R. verniciflua* from Japan and exported to China in the 15th century [21]. It is also reported that Ryukyu Kingdom planted the lacquer trees: *R. verniciflua* in its territory [22]. These reports are consistent with this result.

References

[1] K. Nagase, Toso to Toryo 337 (1981) 66.
[2] Y. Abe, Shitsugeinyuumon, Kougeishuppan, Tokyo, 1987.
[3] K. Taneda, Mokuzaikougyou 40 (1985) 10.
[4] T. Miyakoshi, K. Nagase, T. Yoshida, Urushikagakunoshinpo, IPC, Tokyo, 1999.
[5] M. Kühlenthal, Japanische und europäische Lackarbeiten, Arbeitshefte des Bayerischen Landesamtes für Denkmalpflege, München, 96 (2000).
[6] S. Kobayashi, Gendai Kagaku 7 (2003) 28.
[7] J.B. Lambert, J.S. Frye, G.W. Carriveau, Archaeometry 33 (1991) 87.
[8] J. Kumanotani, Polym. Mater. 59 (1988) 278.
[9] N. Niimura, Y. Iijima, T. Miyakoshi, Bunsekikagaku 42 (1993) 605.
[10] N. Niimura, Y. Iijima, T. Miyakoshi, Surf. Interf. Anal. 24 (1996) 193.
[11] N. Niimura, T. Miyakoshi, Surf. Interf. Anal. 29 (2000) 381.
[12] N. Niimura, T. Miyakoshi, Y. Iijima, Anal. Sci. 2001 Supplement 17 (2001) i155.
[13] T. Miyakoshi, S. Kamiya, Urazoesi Bijutsukan Kiyou 10 (2001) 19.
[14] T. Miyakoshi, H. Togashi, Synthesis (1990) 407.
[15] K. Nagase, H. Iwatsuki, Toso to Toryo 441 (1981) 45.
[16] J. Kumanotani, S. Tanaka, T. Matsui, Proc. 12th Int. Conf. Org. Coat. Sci. Technol., 1986, p. 195.
[17] N. Niimura, T. Miyakoshi, J. Onodera, T. Higuchi, J. Anal. Appl. Pyrol. 37 (1996) 199.
[18] N. Niimura, T. Miyakoshi, J. Onodera, T. Higuchi, Rapid Commun. Mass Spectrom. 10 (1996) 1719.
[19] N. Niimura, T. Miyakoshi, J. Mass Spectrom. Soc. Jpn. 51 (2003) 439.
[20] N. Niimura, T. Miyakoshi, Talanta 70 (2006) 146.
[21] H. Arakawa, Y. Tokugawa, Ryukyu Urushikougei, Nihonkeizaishinbunsha, Tokyo, 1977.
[22] Ryukyushikki Kenkyukai, Ryukyushikki 1 (1983) 4.