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Evolved Gas Analysis of a Japanese Lacquer Film

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Abstract

Japanese lacquer is sap of lacquer trees. Since it dries into a tough and brilliant film, it has been used as the coating material for wood and pottery for long time. The structure of the lacquer film, which mainly consists of urushiol polymer, has been studied for several decades, but the detail remains to be solved. In this study, electron ionization and field ionization mass spectrometry were applied to investigate the structure of the film. Analyzing the evolved gas at 320 °C from the surface of the film, we revealed that the urushiol polymer is terminated with 3-pentadecylcatechol. Furthermore, this terminal group and plant gum are concentrated in the surface of the lacquer film.

Keywords: Japanese lacquer, evolved gas analysis, urushiol, field ionization, electron ionization

1. Introduction

Japanese lacquer is sap, which is obtained by tapping lacquer trees in the same way that natural rubber is harvested from rubber trees. The sap is latex composed of urushiol, water, plant gum, glycoprotein and laccase enzyme as shown in Table 1. It dries into a tough film, so it is used as a coating material for wood and pottery [1]. The lacquer film, which is urushiol polymer, is insoluble. Therefore, analytical methods are limited. The evolved gas analysis is one of the methods. Field ionization (FI) mass spectrometry is an effective method for evolved gas analysis, because it preferentially produces molecular ions and, in some cases, protonated molecular ions.

There is less fragmentation in FI than in electron ionization (EI), therefore, FI mass spectrum of evolved gas is simpler than EI mass spectrum [2].

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We previously reported that the thermogravimetry (TG) curve of the lacquer film shows the weight decrease in two stages, i.e., the thermal degradation gradually begins at around 200 °C, and the degradation rate becomes fastest at 400-500 °C [3, 4]. The derivative thermogravimetry (DTG) curve shows two peaks at 320 °C and 470 °C.

The evolved gas at 320 °C contains the thermal degradation product from the surface of the lacquer film [3, 5].

Using EI and FI mass spectrometry, the evolved gas from a Japanese lacquer film at 320 °C was analyzed and two results were compared.

2. Experimental

2.1 Sample

The sample was obtained by coating the sap of *Rhus vernicifera* lacquer tree on glass plates with the traditional pretreatment called Nayashi and Kurome [6]. The film was kept in a humidity-controlled chamber with relative humidity of 70 % at 20 °C for two weeks. It was then removed from the chamber and left to dry in open air at room temperature.

2.2 EI Mass Spectrometry

EI mass spectrometry was carried out with a quadrupole mass spectrometer: JMS- Q1050GC (JEOL Ltd.). An ionization energy was 70 eV.

2.3 FI Mass Spectrometry

FI mass spectrometry was carried out with a time-of-flight mass spectrometer: JMS- T100GCV (JEOL Ltd.). Diameter of the emitter wire was 10 μm and cathode voltage was -10000 V.

3. Results and Discussion

3.1 EI Mass Spectrometry

The EI mass spectrum of the evolved gas from the lacquer film is shown in Fig. 1. The spectrum was complicated because it was consisted of peaks due to the various kinds of fragment ions as well as molecular ions of the thermal degradation products. We compared the observed spectrum to that of the evolved gas from 3-pentadecylcatechol, which is a component of urushiol. The EI mass spectrum is shown in Fig. 2. The molecular ion was detected at *m/z* 320, and the typical fragment ion was detected at *m/z* 123 as the base peak in the mass spectrum. The fragmentation process is shown in Fig. 3 [2, 7, 8]. The molecular ion gives rise to the fragment ion at *m/z* 123 by preferential cleavage at β to the aromatic ring. Both the molecular ion and the fragment ion were also detected in the mass spectrum of the lacquer film. These ions are attributed to 3-pentadecylcatechol, which is a thermal degradation product of the lacquer film. The lacquer was reported to be hardened by laccase-catalyzed oxidative coupling of urushiol and autoxidative cross-linkage of the side chains[9, 10]. In these reactions, saturated side-chains serve as terminal groups of the polymer, whereas active unsaturated side-chains like alkenylcatechol form polymer skeletons. Therefore, 3-pentadecylcatechol is preferentially dissociated out by the thermal degradation from the terminal groups at the lower temperature around 320 °C.

3.2 FI Mass Spectrometry

The FI mass spectrum of the evolved gas from the lacquer film is shown in Fig. 4. The molecular ion of 3-pentadecylcatechol was detected as the base peak at *m/z* 320.3. This result indicates that the gas consists of 3-pentadecylcatechol, which supports the result obtained using the EI mass spectrometry. Several peaks were also detected at the lower *m/z*. These peaks could not be attributed to 3-pentadecylcatechol, because any of these peaks were not detected as fragment peaks in the FI mass spectrum of the evolved gas from 3-pentadecylcatechol. The spectrum is shown in Fig. 5.

Only molecular ion was detected at *m/z* 320.3. In Fig. 4, the peaks at *m/z* 126.0 and 163.1 were identified as the molecular ion of hydroxymethylfurfuraldehyde (*M*m 126.0311 Da) and protonated molecular ion of anhydrosugar (*M*m 163.0601 Da), respectively.

The accurate mass obtained by correcting a mass drift was 126.0318 and 163.0598 Da, respectively. The difference between the accurate mass and the calculated mass was 0.0007 and 0.0003 Da, respectively. The lacquer film is composed of plant gum. The constituent of the plant gum is polysaccharide and its principal constituent sugar is galactose [11]. It has been reported that galactose is thermally degraded to hydroxymethylfurfuraldehyde and anhydrosugar [12]. Therefore, the observed hydroxymethylfurfuraldehyde and anhydrosugar were reasonably identified as thermal degradation products of plant gum. It is concluded that the plant gum is concentrated in the surface of the lacquer film and it is thermally degraded at the lower temperature around 320 °C.

4. Conclusion

From the evolved gas of a Japanese lacquer film at 320 °C, 3-pentadecylcatechol, hydroxymethylfurfuraldehyde and anhydrosugar were detected. The 3-pentadecylcatechol is the thermal degradation product of urushiol polymer, and the hydroxymethylfurfuraldehyde and the anhydrosugar are those of plant gum. It is concluded that urushiol polymer is terminated with 3-pentadecylcatechol. And this terminal group and plant gum are concentrated in the surface of the lacquer film.

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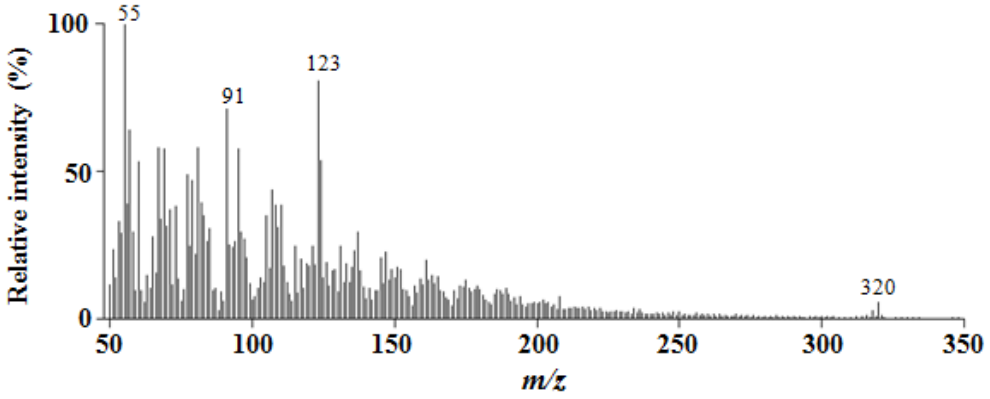

Fig. 1 EI Mass Spectrum of the Evolved Gas from the Lacquer Film

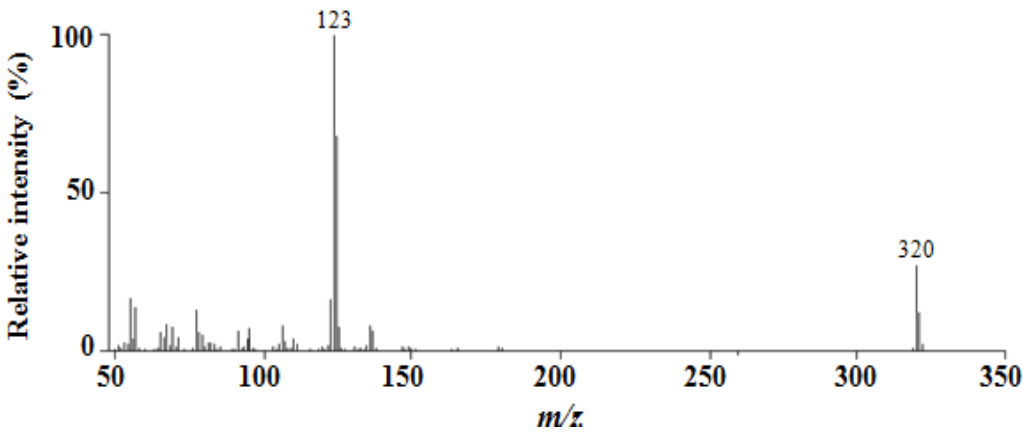

Fig. 2 EI mass Spectrum of the Evolved Gas from 3-Pentadecylcatechol

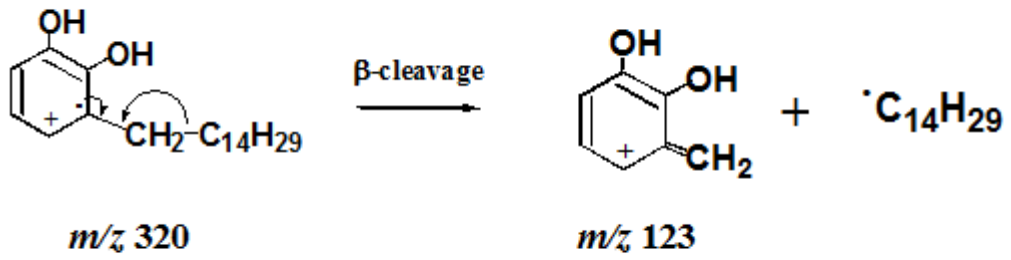

Fig. 3 Fragmentation Process of the Molecular Ion

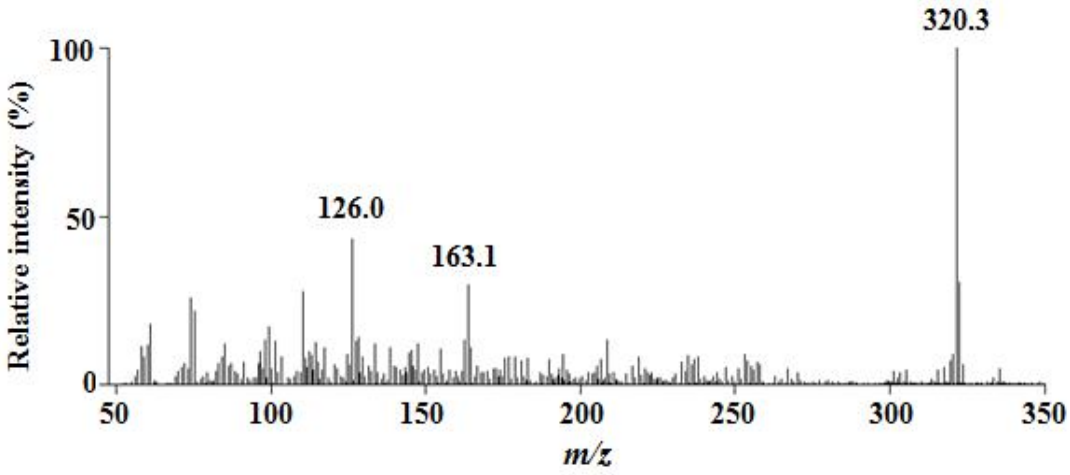

Fig. 4 FI mass Spectrum of the Evolved Gas from the Lacquer Film

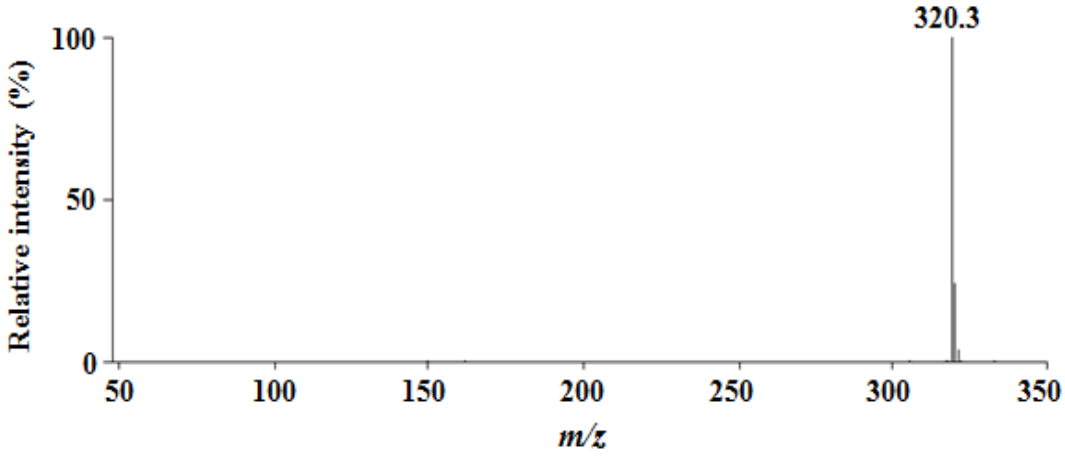

Fig. 5 FI Mass Spectrum of the Evolved Gas from 3-Pentadecylcatechol

Table 1 Composition of sap of *Rhus vernicifera* lacquer

components	%
urushiol	60-65
water	20-25
plant gum (polysaccharide)	5-7
glycoprotein	2-5
laccase enzyme	1-2