

Characterization of natural resin shellac by reactive Pyrolysis – gas chromatography

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Abstract: Reactive pyrolysis gas chromatography (Py – GC) in the presence of an organic alkali, tetramethylammonium hydroxide ((CH₃)₄NOH, TMAH), was applied to the compositional analysis of natural resin shellac. Furthermore, discriminative analysis among shellac samples produced in India and Thailand was carried out by means of the principal component analysis (PAC) on the basis of the chemical composition of all the resin acid components determined by Py – GC.

Key words: Py – GC; natural resin shellac; PCA

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Shellac is one of the thermosetting resins of animal origin secreted by the lac insect *Kerria lacca* which parasitically grows on some types of trees such as mulberries commonly found in India, Thailand, Myanmar and south area of China. Shellac has been used as thermoplastics, adhesives and sealants, insulating materials and coating materials in various fields such as industrial material, medicine and food ingredient due to its various unique properties such as thermoplasticity, oil – resistibility, cohesiveness and insulating ability along with its non – poisonous nature^[1]. Shellac is provided as a refined form of the stic – lac resin (raw shellac, just collected from twigs of the trees) consisting of resin (70 ~ 80%), wax (6 ~ 7%), coloring matter (4 ~ 8%) and others (15 ~ 25%) such as debris and moisture. The resin portion constituting the backbone of shellac is a complex mixture of polyesters consisting of a number of closely related sesquiterpenic acids of the cedrene skeleton, mainly jararic acid and laccijalaric acid, and hydroxy – fatty acids, mainly threo – aleuritic acid, which can be separated into about 30% of soft resin (single ester) and about 70% of hard resin (polyesters consisting of several resin acid components)^[1~3]. The chemical composition of shellac which affects its mechanical and thermal properties often varies to some extent depending on nature of the host trees on which the insect grows, the species of the insect and the environmental conditions. Therefore, it is important to know the subtle differences in the chemical composition of shellac.

Various analytical techniques such as chemical analysis, and chromatographic and spectrometric methods have been

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applied to semi-quantitative determination of shellac resin.^[4-9] In these reports, however, cumbersome pretreatments such as chemical decomposition, derivatization and/or solvent extraction were inevitably utilized to separate the resin constituents prior to the final analytical measurements. Recently, Py-GC/MS in the presence of an organic alkali, tetramethylammonium hydroxide ((CH₃)₄NOH, TMAH) has been successfully applied to the characterization of small amounts of natural products consisting of various terpenic acids^[10,11], the sensitive determination of rosin sizing agents and fortified rosin-glycerin ester sizing agents in paper^[12,13] and the lipid analysis of zooplankton individuals^[14,15] without using any tedious pretreatments.

In this work, reactive Py-GC in the presence of TMAH was applied to the compositional analysis of natural resin shellac. Furthermore, discriminative analysis among shellac samples produced in India and Thailand was carried out by means of the principal component analysis (PCA) on the basis of the chemical composition of all the resin acid components determined by Py-GC.

1 Materials and methods

1.1 Materials

Eight shellac samples formed from stick-lac gathered in India and Thailand were used in this study. All the shellac samples were cryo-milled into a fine powder (less than 60 mesh) by a freezer mill (SPEX 6700) prior to Py-GC measurements in order to improve the efficiency of the reactive pyrolysis.

An aqueous solution (25% wt/wt) of tetramethylammonium hydroxide (TMAH), supplied by Tama Chemicals (Tokyo, Japan), were used as the reagent for the reactive pyrolysis.

1.2 Reactive Py-GC Condition

A vertical microfurnace pyrolyzer (GP1018, Yanaco, Kyoto, Japan) was directly attached to a gas chromatograph (HP 5890, Hewlett-Packard, Avondale, PA, USA) equipped with a flame ionization detector (FID). About 90 (g of shellac sample and 2 μ L of the TMAH solution taken in a platinum sample cup were introduced into the heated center of the pyrolyzer under the flow of helium carrier gas. The relatively low pyrolysis temperature of 400°C was used to suppress the competitive ordinary pyrolysis at higher temperatures. A fused silica capillary column (Hewlett-Packard Ultra 1, 25 m \times 0.2 mm i.d.) coated with polydimethylsiloxane (0.33 μ m film thickness), immobilized by chemical cross-linking was used. The flow rate of 50 mL/min of carrier gas at the pyrolyzer was reduced to 1.0 mL/min at the capillary column by means of a splitter. Identification of the peaks on the resulting pyrograms was carried out by use of a GC/MS system (JEOL AM-II 150) to which the same pyrolyzer was also attached. For the MS measurement, ionization was carried out by electron impact (EI) at 70 eV.

1.3 Principal Component Analysis (PCA)

In order to distinguish shellac samples produced in different origins by considering all the acid components observed on the pyrograms, the resulting compositional data were processed by use of the principal component analysis (PCA) software, Ein Sight (InfoMetrix).

2 Results and Discussion

Figure 1 shows typical pyrograms of Indian shellac at 400°C, obtained without adding TMAH(a) and in the presence of TMAH aqueous solution(b). In the pyrogram of Figure 1(a), only a series of very weak and broad peaks of terpenic acids and wax components were observed. Furthermore, no peak of the hydroxy fatty acids such as aleuritic acid was observed mainly due to their extremely high polarity. On the contrary, a series of sharp peaks due to methyl derivatives of shellac constituents were observed in Figure 1(b) with far better resolution and higher sensitivity after the elution of the reagent related peaks. As shown in this figure, methyl derivatives of shellac constituents were formed as a result of the selective hydrolysis of ester bonding followed by simultaneous methylation of the carbonyl and hydroxyl groups. More-

over, not only characteristic products of the terpenic acids, such as laccijalaric and jalaric acids, and aleuritic acids, but also various minor $C_{14} - C_{16}$ straight chain fatty acids, hydroxy - fatty acids and wax components such as $C_{28} - C_{34}$ even - numbered straight - chain alcohols were also observed as their methyl derivatives.

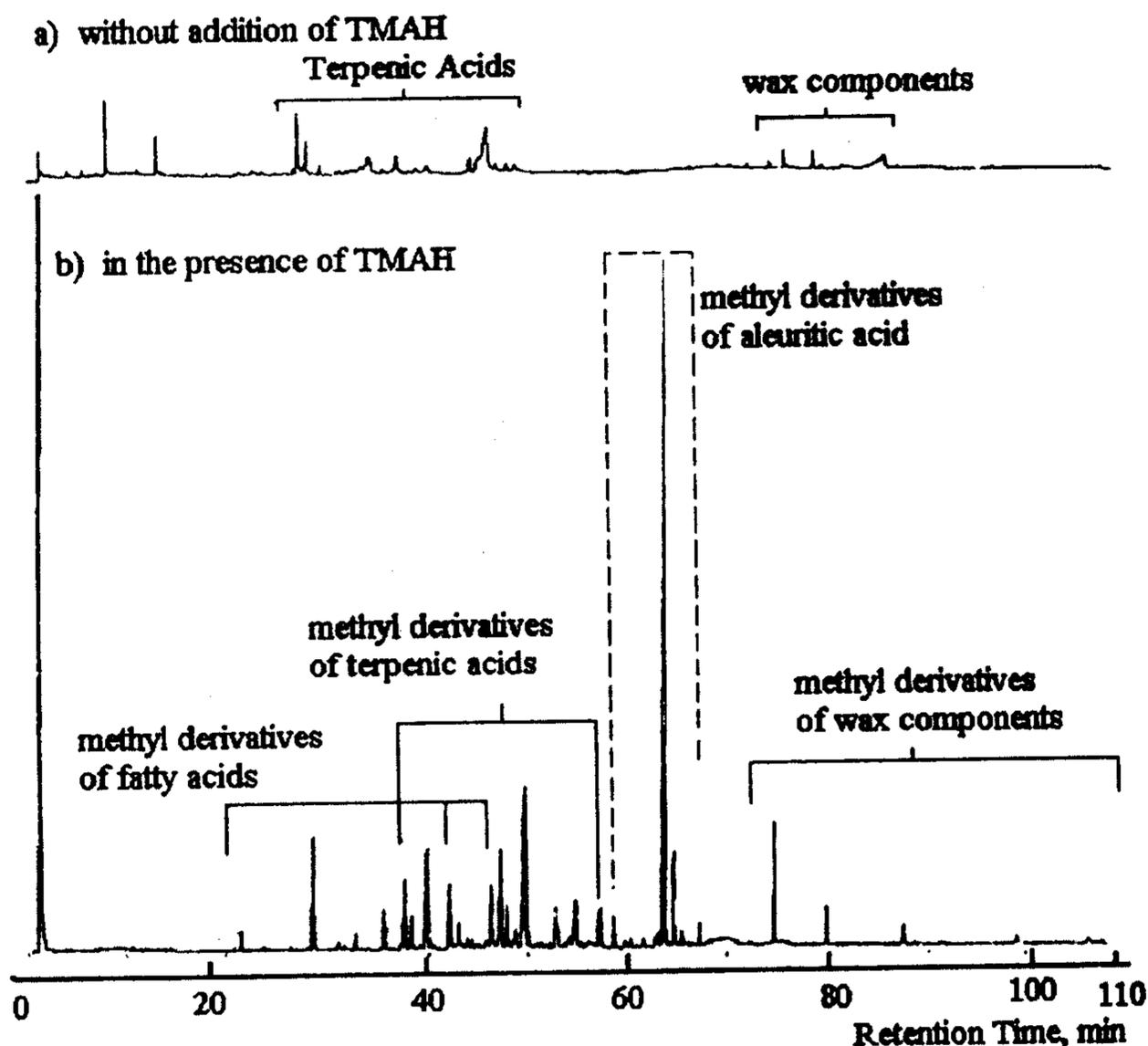


Figure 1 Typical pyrograms of Indian shellac at 400°C (a) without addition of TMAH and (b) in the presence of TMAH aqueous solution.

Chemical composition of resin acid for each shellac sample was determined on the basis of the peak intensities on the pyrograms obtained during the reactive pyrolysis in the presence of TMAH aqueous solution. The distributions of the total terpenic acids, aleuritic acid and the other fatty acids are fairly similar among these eight samples regardless of the difference in their origin. On the other hand, the relative amounts of several constituents of terpenic acids such as laccijalaric and jalaric acids, and minor constituents of aliphatic and hydroxy - fatty acids proved to be different to some extent between Indian and Thailand shellac. The reproducibility of this method was less than 2% of the relative standard deviation for the estimated distributions for three repeated runs.

In order to distinguish the shellac samples of different origin clearly, the PCA method was applied in which the obtained mol% distributions of all the acidic components (14 components)

for eight shellac samples produced in India and Thailand were used as the data base after converting them into the deviation values. The contributory rates (dispersion) of the first, second and third principal components obtained were 85.6,

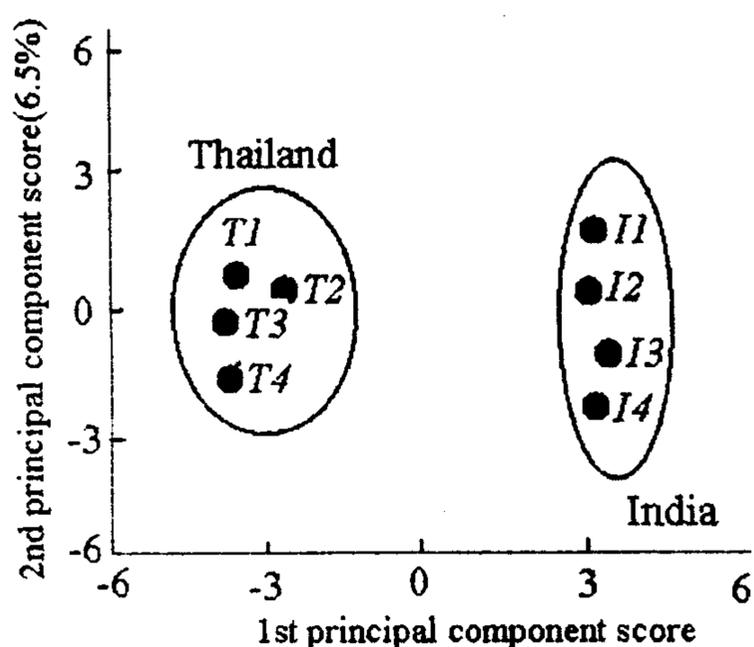


Figure 2 Discriminative analysis among shellac samples produced in different country

6.5 and 4.3%, respectively. Figure 2 shows the relationship between the first and second principal component scores for eight shellac samples from India and Thailand. As shown here, these shellac samples are clearly divided into two different groups according to their origin.

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天然树脂紫胶的热裂解 - 气相色谱特性

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摘要: 本文研究了有机碱试剂, 氢氧化四甲铵 (tetramethylammonium hydroxide TMAH), 共存下的反应热裂解气相色谱 (Py-GC) 应用于天然树脂紫胶的化学组成分析。并在反应 Py-GC 测得的化学组成的基础上, 应用主成分分析 (principal component analysis, PCA) 对印度和泰国产紫胶进行产地识别分析。

关键词: 热裂解气相色谱; 天然树脂紫胶; 主成分分析