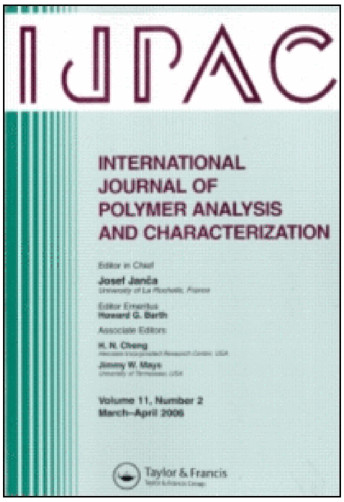

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Structural Characterization of Cashew Resin Film Using Two-Stage Pyrolysis-Gas Chromatography/Mass Spectrometry

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Structural Characterization of Cashew Resin Film Using Two-Stage Pyrolysis-Gas Chromatography/Mass Spectrometry

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Technical cashew nut shell liquid (CNSL) was analyzed to investigate its constituents using gas chromatography/mass spectrometry (GC/MS). The results showed that it consists of cardanols and cardols but not 2-methylcardol. After the addition of hexamethylenetetramine to technical CNSL, the mixture was polymerized into the cashew resin film by autoxidation. The film was analyzed using two-stage pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). It was found that the cashew resin is terminated with saturated cardols and cardanols after the pyrolysis at 400°C. This pyrolysis effectively identifies the cashew resin from the other resins and saps. Furthermore, pyrolysis at 500°C revealed that the autoxidative side-chain/side-chain C-C coupling accelerated the cross-linking of trienyl- and dienylcardanols during polymerization.

Keywords: Cashew; CNSL; Py-GC/MS; Pyrolysis; Resin

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Cashew nut shell liquid (CNSL) is a source of natural resin[1] and is obtained from the shell of the cashew nut[2]. The cashew tree, i.e., *Anacardium accidentale linn*, grows in Brazil, India, Tanzania, the Philippines, and other tropical countries[2]. A large amount of CNSL is produced in these countries inexpensively[2]; therefore, various industrial applications of CNSL are available[3]. For example, cashew resin, which is a polymer of CNSL, is used as a coating material for decoration[4]. A new functional polymer has been developed by mixing CNSL and synthesized resin, and its use as an industrial coating and building material has been discussed[5–21].

The composition of natural CNSL was determined by preparative thin-layer chromatography (TLC) using a multiple development procedure, and the presence of anacardic acid up to 71.7% along with cardol (18.7%), cardanol (4.7%), 2-methylcardol (2.7%), and less polar substances (2.2%) was reported[22]. The structures of these components are shown in Scheme 1. However, the raw CNSL, which is oozed from the shell by the general methods of hot-oil or roasting, contains only 3%–9% of anacardic acid. The observed small content of anacardic acid in the raw CNSL has been attributed to the decarboxylation of anacardic acid during heat treatment.

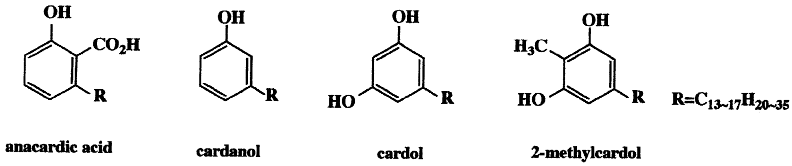
In this study, technical CNSL, which was obtained from raw CNSL by distillation, was analyzed in order to investigate its constituents using gas chromatography/mass spectrometry (GC/MS). Hexamethylenetetramine was then added to the technical CNSL, and the mixture was polymerized into a cashew resin film by heating. This film was analyzed using two-stage pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), and its structure was studied.

EXPERIMENTAL

Analysis of Technical CNSL Using GC/MS

Sample

Technical CNSL was obtained from raw CNSL by distillation.



SCHEME 1 Components of natural CNSL.

GC/MS Measurements

GC/MS measurements were carried out using an HP6890 (HP Ltd.) gas chromatograph and a JMS-AMII (JEOL Ltd.) mass spectrometer. A stainless steel capillary column (0.25 mm i.d. × 30 m) coated with 0.25 µm thick Ultra Alloy 1 (methylsilicone 100%) was used for separation. The GC oven was programmed at a constant rate of temperature rise of 20°C/min in a range from 40° to 330°C. The mass spectrometer ionization energy was 70 eV (EI-MS).

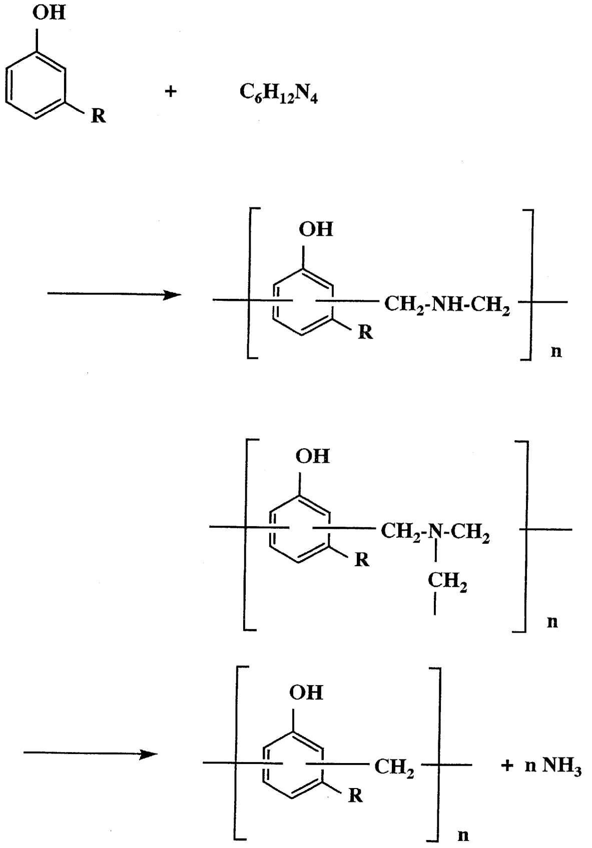
Analysis of Cashew Resin Film Using Py-GC/MS

Sample

Hexamethylenetetramine was added to the technical CNSL at lower temperatures to yield benzylamine derivative. A secondary reaction occurs at higher temperatures involving the reaction of excess technical CNSL with benzylamines to form a methylene cross-linked structure with the evolution of ammonia. Metallic soap of manganese and cobalt was added to the methylene cross-linked structure to yield a cashew resin film. The synthetic pathways between cardanol and hexamethylenetetramine are shown in Scheme 2.

Py-GC/MS Measurements

Py-GC/MS measurements were carried out using a PY-2010D (Frontier Lab.) vertical microfurnace-type pyrolyzer, an HP6890 (HP Ltd.) gas chromatograph, and a JMS-AMII (JEOL Ltd.) mass spectrometer. A stainless steel capillary column (0.25 mm i.d. × 30 m) coated with 0.25 µm thick Ultra Alloy PY-2 (methylsilicone 100%) was used for separation. The He carrier gas flow of 50 mL/min at the pyrolyzer was reduced to 1 mL/min at the capillary column by using a splitter. The sample (0.5 mg) was placed in a platinum sample cup and the cup was set on the top of the pyrolyzer kept at near room temperature. The sample cup was introduced into the furnace at 400°C, and then the temperature programming of the GC oven was started. The GC oven was programmed at a constant rate of temperature rise of 20°C/min in a range from 40° to 330°C. After the sample cup was kept in the furnace for 30 min, it was retracted to the initial position. The furnace was then reset to 500°C. After the first pyrogram was recorded, the sample cup was dropped into the furnace at 500°C, and the temperature program of the GC oven was restarted. All pyrolysis products were identified by mass spectrometry. The mass spectrometer ionization energy was 70 eV (EI-MS).



SCHEME 2 Synthetic pathways between cardanol and hexamethylenetetramine.

RESULTS AND DISCUSSION

Analysis of Technical CNSL Using GC/MS

The technical CNSL was analyzed using GC/MS and the results are shown in Figure 1. The chromatogram (m/z 108) shows peaks 1 to 6 at retention times of 12 min 2 s, 12 min 47 s, 12 min 50 s, 12 min 52 s, 12 min 54 s, and 13 min 38 s, respectively. They were identified as 3-tridecylphenol (MW 276), 3-pentadecatrienylphenol (MW 298), 3-pentadecadienylphenol (MW 300), 3-pentadecenylphenol (MW 302), 3-pentadecylphenol (MW 304), and 3-heptadecenylphenol (MW 330), respectively, by comparison with analysis and mass spectra of reference

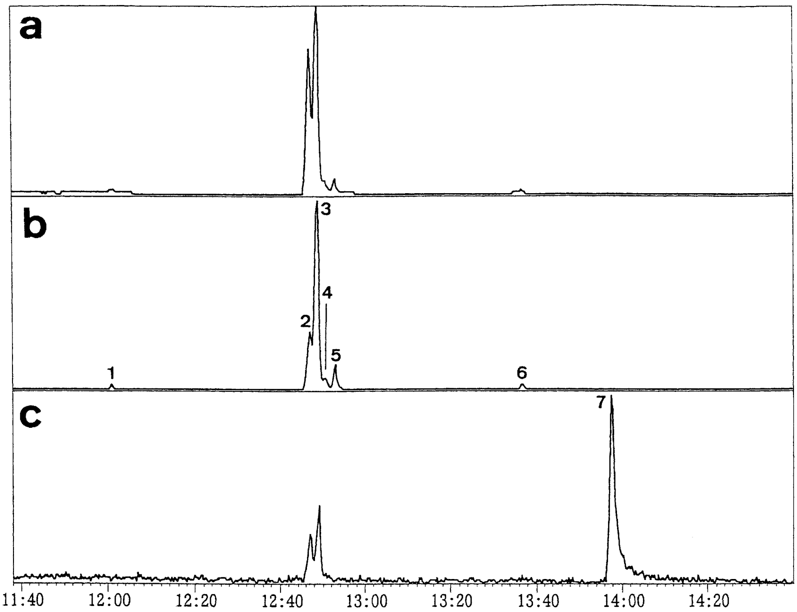


FIGURE 1 TIC and mass chromatograms of technical CNSL. (a) TIC; (b) mass chromatogram (m/z 108), 1: 3-tridecylphenol (MW 276), 2: 3-pentadecatrienylphenol (MW 298), 3: 3-pentadecadienylphenol (MW 300), 4: 3-pentadecenylphenol (MW 302), 5: 3-pentadecylphenol (MW 304), 6: 3-heptadecenylphenol (MW 330); (c) mass chromatogram (m/z 124), 7: 5-pentadecylresorcinol (MW 320).

components (Figure 2). These components are cardanols. In addition, peak 7 was detected at retention time of 13 min 59 s in the mass chromatogram (m/z 124) and was identified as 5-pentadecylresorcinol (MW 320) by comparison with a standard. This composite ratio was calculated from the peak area as 3-tridecylphenol: 0.6%; 3-pentadecatrienylphenol: 39.9%; 3-pentadecadienylphenol: 52.7%; 3-pentadecenylphenol: 1.9%; 3-pentadecylphenol: 2.8%; 3-heptadecenylphenol: 1.7%; and 5-pentadecylresorcinol: 0.4%.

As an example, TIC and mass spectra of synthesized 3-pentadecylphenol and 5-pentadecylresorcinol are shown in Figures 3 and 4, respectively. The TIC shows the peaks due to 3-pentadecylphenol and 5-pentadecylresorcinol at retention times of 12 min 52 s and 13 min 59 s, respectively. These retention times are the same as those of peaks 4 and 7, respectively. Additionally, the mass spectrum of 3-pentadecylphenol shows the peak of phenylcation (m/z 77), which is the typical fragment ion peak of aromatics. Furthermore, the typical fragment ion (m/z 108)

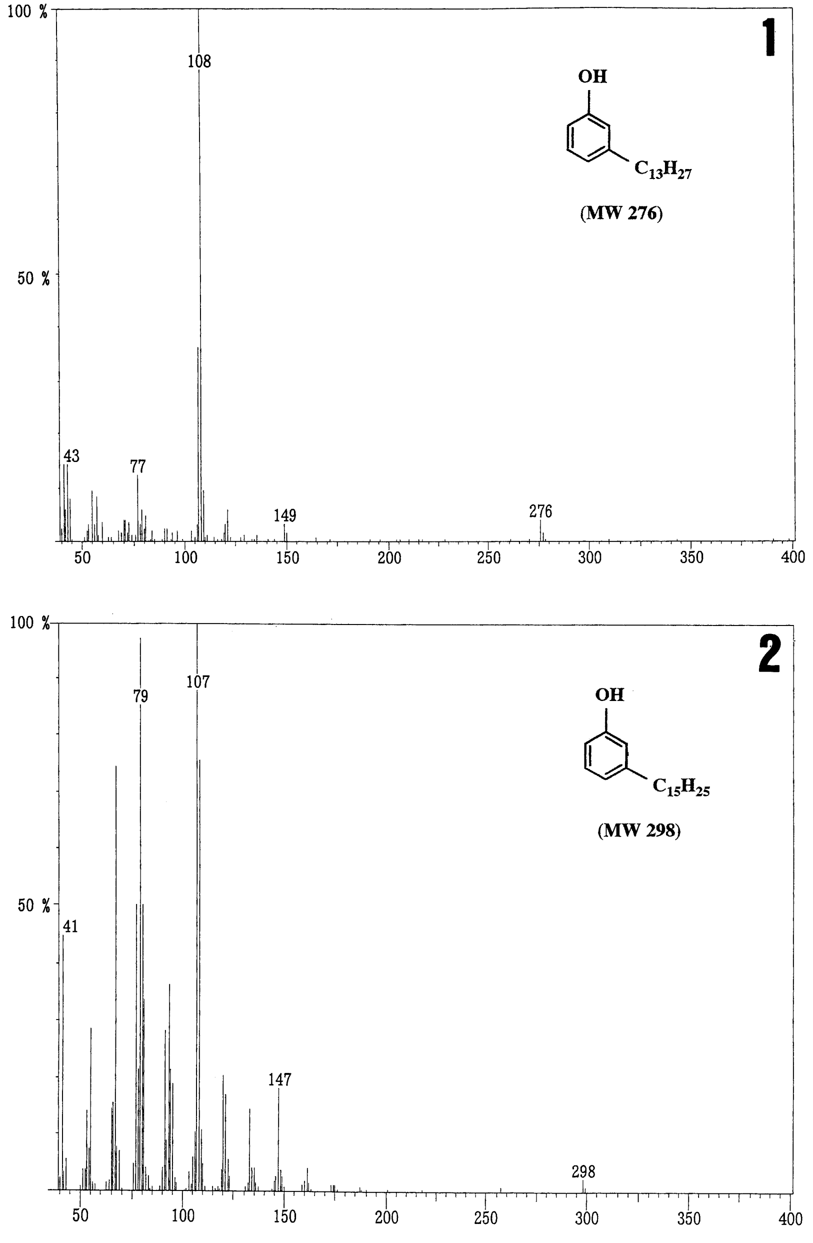


FIGURE 2 Mass spectra of peaks 1–7. 1: 3-tridecylphenol, 2: 3-pentadecatrienylphenol, 3: 3-pentadecadienylphenol, 4: 3-pentadecamonoenylphenol, 5: 3-pentadecylphenol, 6: 3-heptadecenylphenol, 7: 5-pentadecylresorcinol.

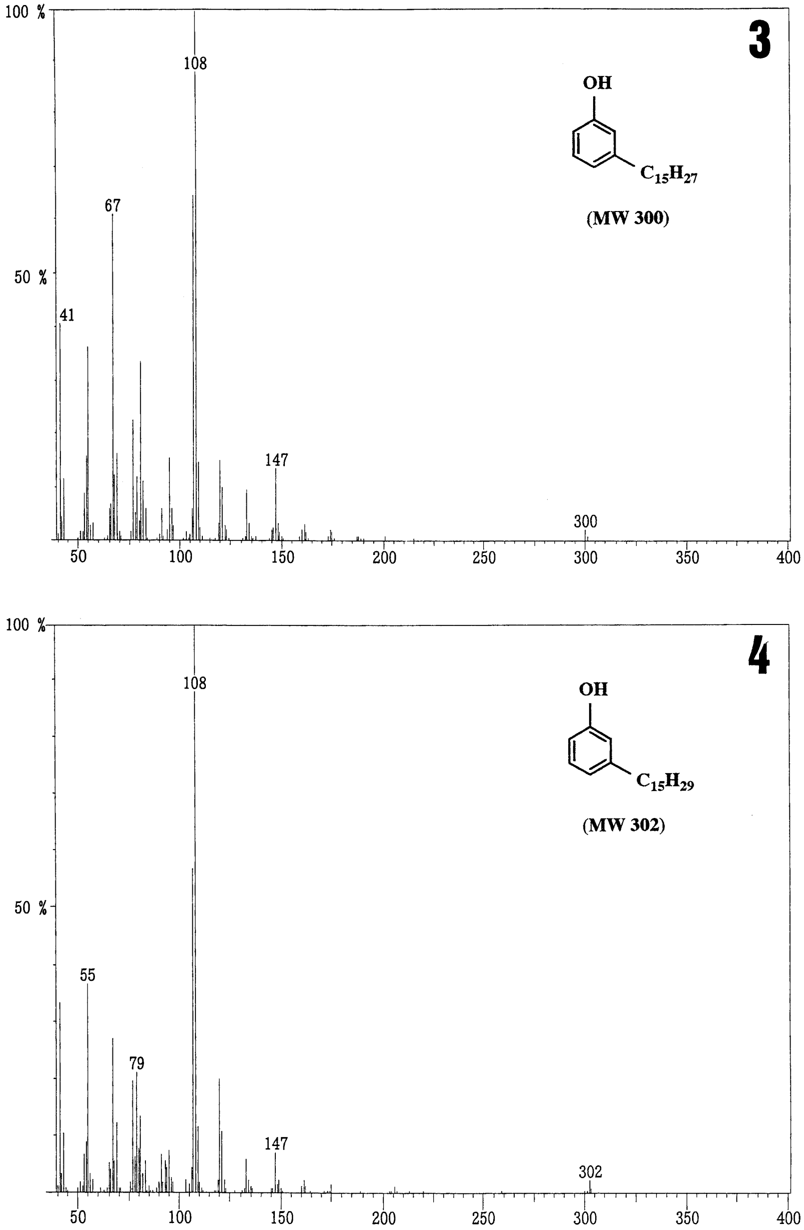


FIGURE 2 (*Continued.*)

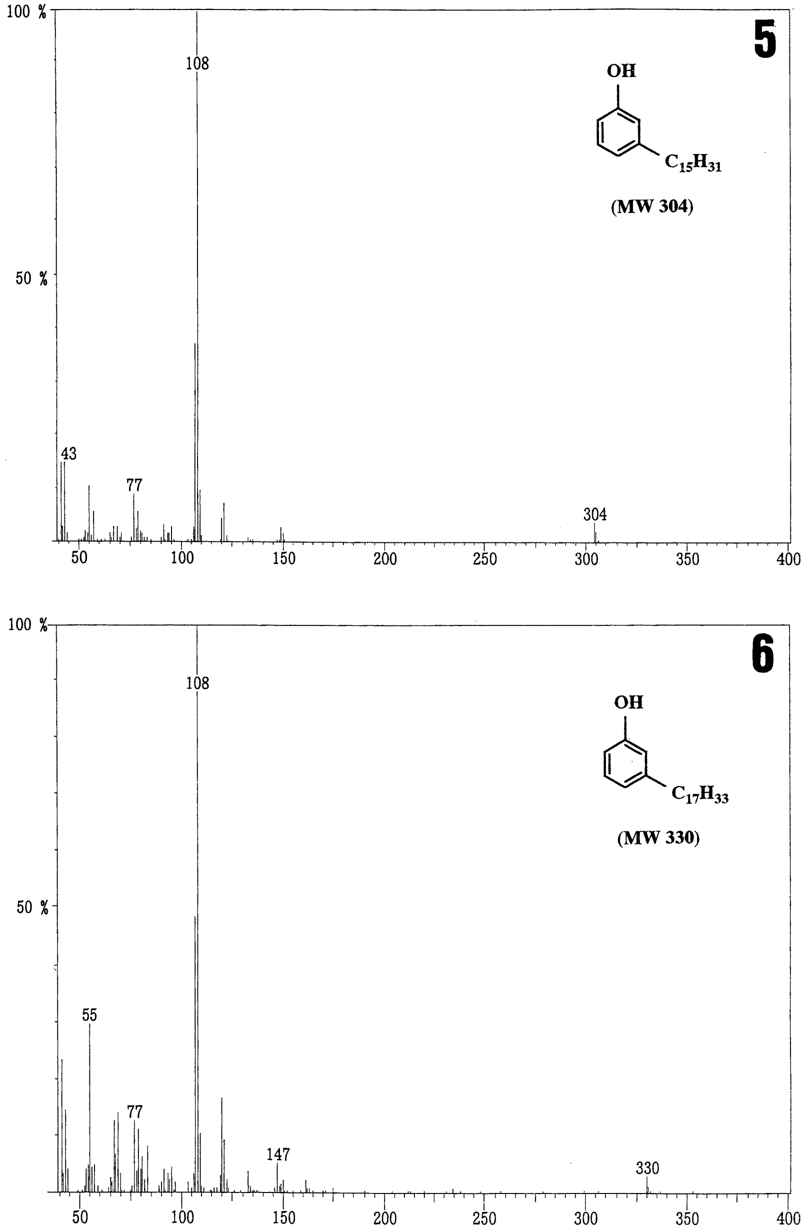


FIGURE 2 (*Continued.*)

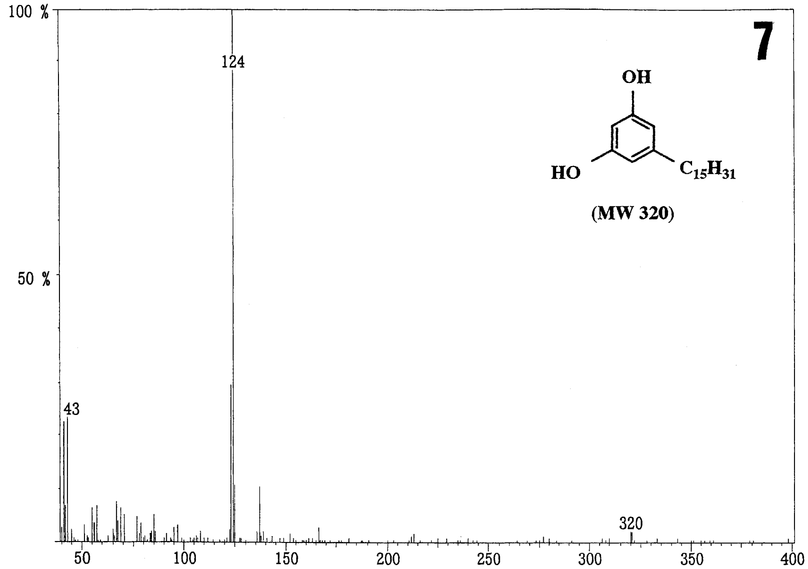


FIGURE 2 (*Continued.*)

peak of alkylphenol as the base-ion peak and the molecular ion (m/z 304) peak as is true of the mass spectrum of peak 5 shown in Figure 1. The result described clearly shows that the technical CNSL consists of cardanols and cardols but not of 2-methylcardol.

Analysis of Cashew Resin Film Using Py-GC/MS

Pyrolysis at 400°C

TIC and mass chromatograms (m/z 108, 320) of cashew resin film obtained by pyrolysis at 400°C are shown in Figure 5. The mass chromatogram (m/z 108) shows the peaks 1–17. These peaks were identified as alkenylphenols and alkylphenols having C1-C17 side chains. As an example, the mass spectra of peak 6 identified as 3-hexenylphenol (MW 176) and 3-hexylphenol (MW 178) are shown in Figure 6. Each spectrum shows the base ion peak at m/z 108, which corresponds to the typical fragment ion of an alkylphenol, together with the molecular ion peaks at m/z 176 and 178. The condensation products of cardanol and hexamethylenetetramine are pyrolyzed into these alkenylphenols and alkylphenols formed by the scission of methylene bonding and the random scission of side chain of cardanol. The random scission of the alkyl side chain is known to produce an α-olefin and *n*-paraffin.

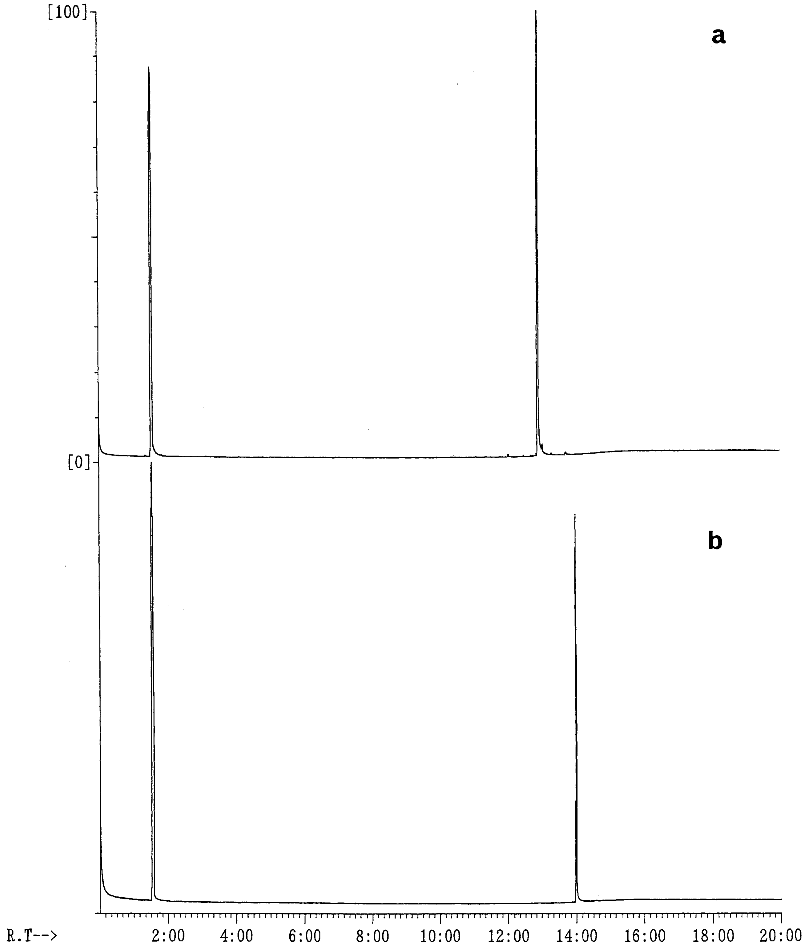


FIGURE 3 TIC of the synthesized 3-pentadecylphenol and 5-pentadecylresorcinol. (a) 3-pentadecylphenol; (b) 5-pentadecylresorcinol.

The relative peak intensity of peak 15, which is identified as 3-pentadecenylphenol and 3-pentadecylphenol, is the highest among the peaks. This can be attributed to the preferential cleavage of the terminal group of the cashew resin film. The autoxidation mechanism for the polymerization of urushiol, which is a monomer of the oriental lacquer, can explain this result. It was reported that urushiol, whose side chain is an alkene or alkane like cardanol and cardol, polymerizes into the

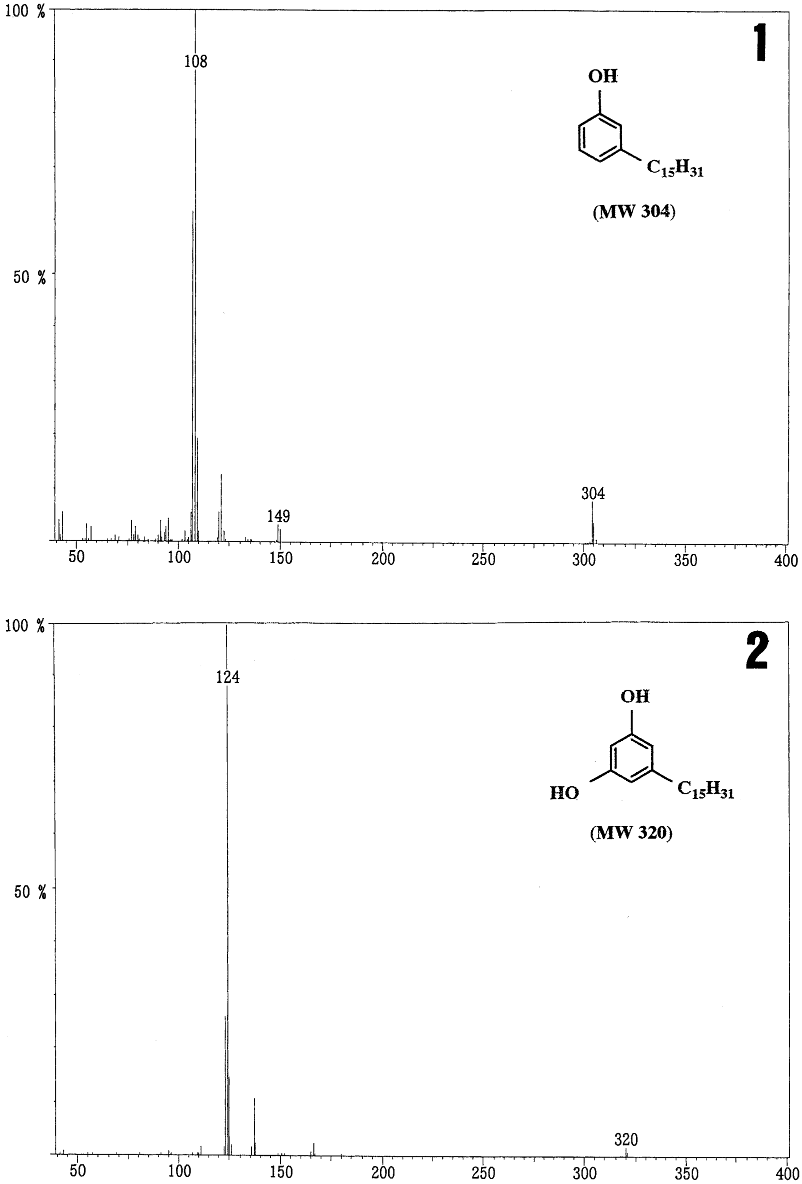


FIGURE 4 Mass spectra of 3-pentadecylphenol and 5-pentadecylresorcinol. 1: 3-pentadecylphenol (MW 304); 2: 5-pentadecylresorcinol (MW 320).

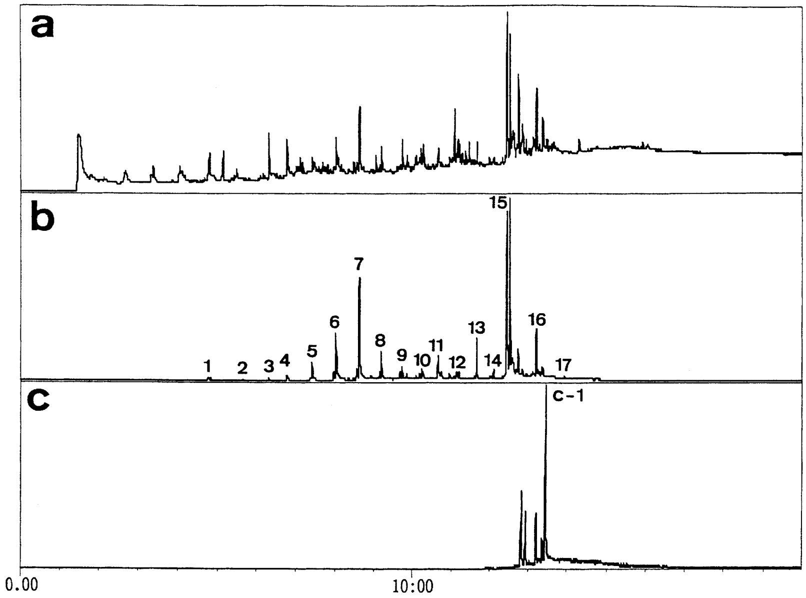


FIGURE 5 TIC and mass chromatograms of cashew resin film obtained by pyrolysis at 400°C. (*a*) TIC; (*b*) mass chromatogram (m/z 108), 1: 3-methylphenol; 2: 3-ethenylphenol, 3-ethylphenol; 3: 3-propenylphenol, 3-propylphenol; 4: 3-butenylphenol, 3-butylphenol; 5: 3-pentenylphenol, 3-pentylphenol; 6: 3-hexenylphenol, 3-hexylphenol; 7: 3-heptenylphenol, 3-heptylphenol; 8: 3-octenylphenol, 3-octylphenol; 9: 3-nonenylphenol, 3-nonylphenol; 10: 3-decenylphenol, 3-decylphenol; 11: 3-undecenylphenol, 3-undecylphenol; 12: 3-dodecenylphenol, 3-dodecylphenol; 13: 3-tridecenylphenol, 3-tridecylphenol; 14: 3-tetradecenylphenol, 3-tetradecylphenol; 15: 3-pentadecenylphenol, 3-pentadecylphenol; 16: 3-hexadecenylphenol, 3-hexadecylphenol; 17: 3-heptadecenylphenol, 3-heptadecylphenol; (*c*) mass chromatogram (m/z 320), C-1: 5-pentadecylresorcinol (MW 320).

oriental lacquer film by the autoxidation of the side chains[23]. At the first step of autoxidation, urushiol is oxidized into peroxide and alkoxy radical, and finally, these precursors produce urushiol side-chain/side-chain C-O-C coupling polymers and C-C coupling polymers. The cardanol and cardol should be autoxidized and produce side-chain/side-chain C-O-C coupling polymer and C-C coupling polymer because the side chains of cardanol and cardol are alkanes or alkenes like urushiol[24]. Furthermore, the autoxidative reaction rate of trienylcardanol and cardol is the fastest, and that of dienylcardanol and cardol is the second fastest, while that of monoenyl and saturated cardanol and cardol is the slowest. Therefore, the cashew resin film is terminated by

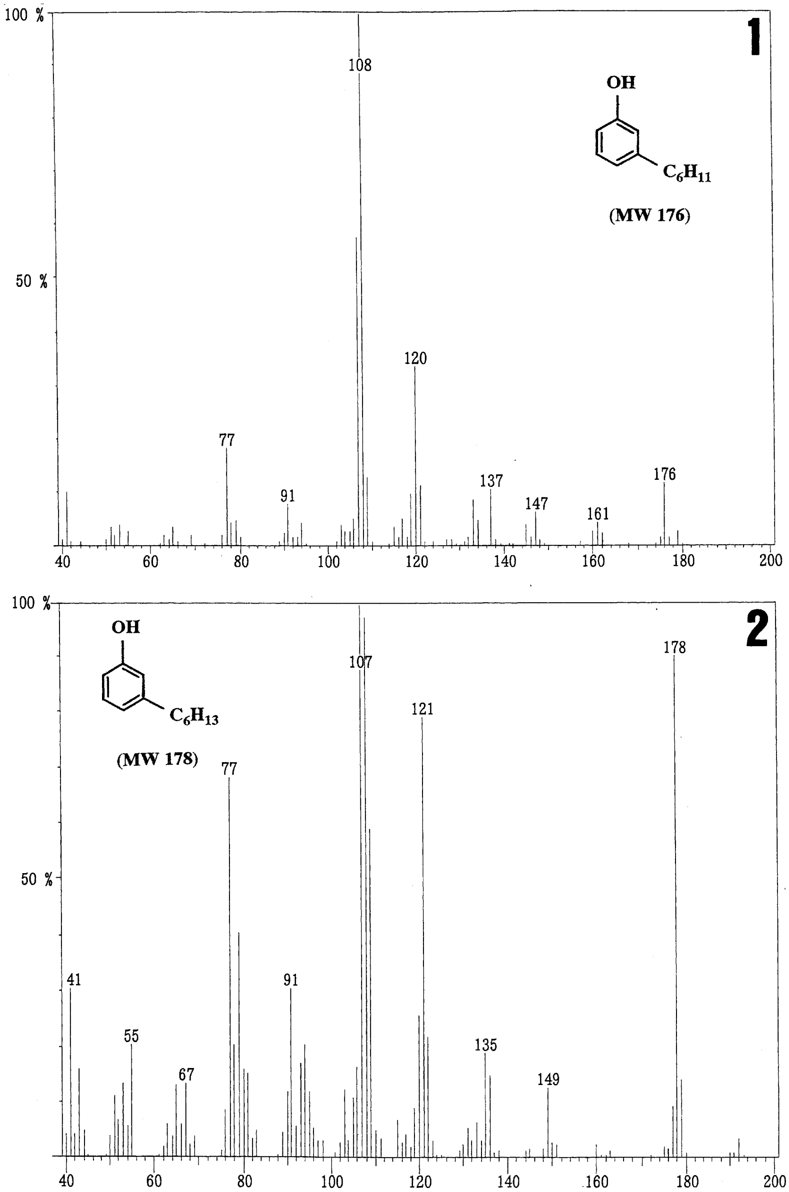
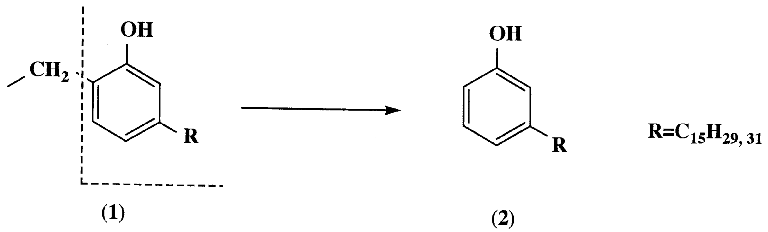


FIGURE 6 Mass spectra of peak 6. 1: 3-hexenylphenol; 2: 3-hexylphenol.



SCHEME 3 Pyrolysis mechanism of the terminal group. (1) Terminal groups of the cardanol polymer; (2) 3-pentadecenylphenol and 3-pentadecylphenol.

monoenyl and saturated cardanol and cardol. The highest yield of 3-pentadecenylphenol and 3-pentadecylphenol can be attributed to the preferential cleavage of these terminal groups.

The pyrolysis mechanism of these terminal groups is shown in Scheme 3. However, the mass chromatogram (m/z 320) shows the peak C-1 as shown in Figure 5. This is identified as 5-pentadecylresorcinol by the mass spectrum shown in Figure 7. The base ion peak at m/z 124 is the typical fragmention peak of an alkyl resorcinol and the molecular ion peak is detected at m/z 320. 5-Pentadecylresorcinol is also the pyrolysis product of the terminal group of the cashew resin film, because 5-pentadecylresorcinol is the main component of the saturated cardol. This pyrolysis is effective for distinguishing the cashew resin from the other resins and saps.

Pyrolysis at 500°C After Pyrolysis at 400°C

The cashew resin film was pyrolyzed at 500°C after pyrolysis at 400°C. The TIC and mass chromatograms (m/z 55, 57, 108) obtained by pyrolysis are shown in Figure 8. Peak pairs of C5 to C20 were detected in the mass chromatograms (m/z 55, 57). As an example, the mass spectra of C14 are shown in Figure 9. The larger peak on the left side in the peak pair C14 was identified as 1-tetradecene by the mass spectrum shown in Figure 9-1, as the typical fragmention peaks of alkene were detected at m/z 55 and 83 and the molecular ion peak was detected at m/z 196. In addition, the smaller ion peak on the right side was identified as 1-tetradecane by the mass spectrum shown in Figure 9-2. The typical fragment ion peaks of alkane were detected at m/z 57 and 85 and the molecular ion peak was detected at m/z 198 in the mass spectrum. The other peak pairs were identified as alkenes and alkane (C5-C20 hydrocarbons) by mass spectra. These alkenes and alkanes are attributed to the terminal groups of cashew resin film, i.e., the monoenyl and saturated cardol and cardanol. The alkene and alkane (C5-C17 hydrocarbons) were produced from the side chains of the monoenyl and saturated cardol and

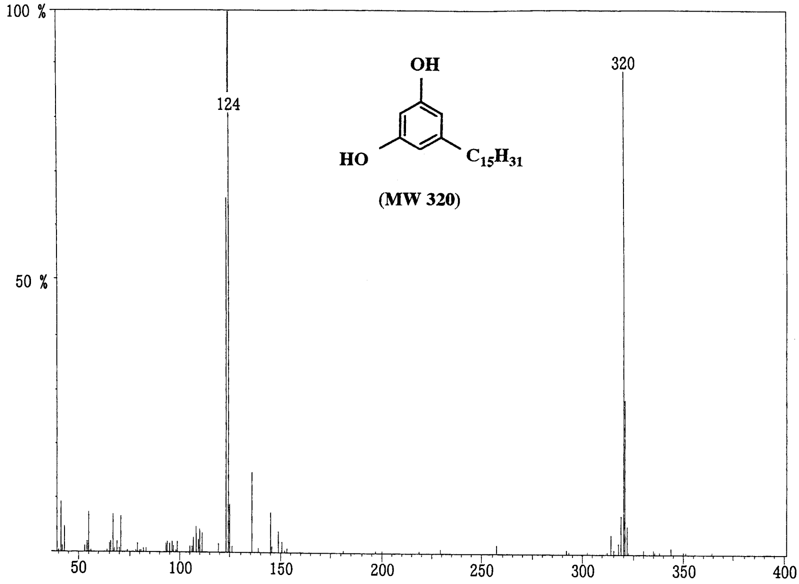


FIGURE 7 Mass spectrum of peak C-1. C-1: 5-pentadecylresorcinol.

cardanol by random scission. The relative peak intensity of 1-tetradecene and tetradecane (C14 hydrocarbons) is the highest among the peaks. However, the degradation pathway generally proposed for macromolecular-bound aromatic moieties is cleavage of the carbon-carbon bond between the α- and β-carbon atoms ("β-scission") of the side chain through which the aromatic nucleus is linked[25–27]. Therefore, the reason why the relative peak intensity of 1-tetradecene and tetradecane (C14 hydrocarbons) is the highest among these peaks is as follows. The main components of cardol and cardanol have C15 side chains, and the terminal groups of the cardol polymers and cardanol polymers are monoenyl and saturated side chains of these components. The highest yield of the C14 hydrocarbons can be attributed to the preferential cleavage of the terminal alkyl- and monoenyl side chains at the β-position to the aromatic ring, as shown in Scheme 4.

The alkenes and alkanes whose carbon chains are longer than C18 are attributed to the cardol and cardanol polymers, in which C-C coupling takes place between their side chains. It was already described that cardol and cardanol polymerize into the cashew resin by the autoxidation of the alkenyl side chains. The side chains of these cardol and cardanol polymers must be longer than C18. Therefore the alkenes and alkanes whose carbon chains are longer than C18 are pyrolysis products of these polymers.

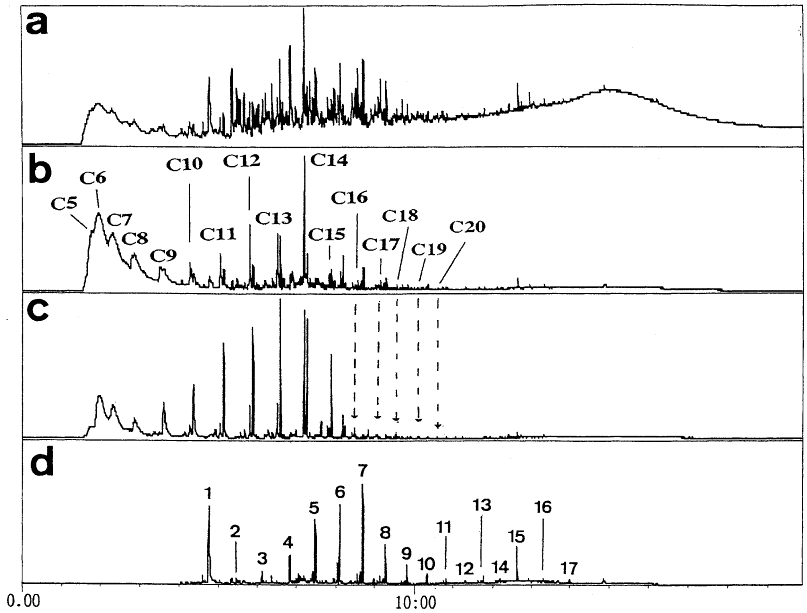


FIGURE 8 TIC and mass chromatograms obtained by pyrolysis at 500°C. (*a*) TIC; (*b*) mass chromatogram (m/z 55); (*c*) mass chromatogram (m/z 57), C5: pentane; C6: 1-hexene; C7: heptane; C8: 1-octene, octane; C9: 1-nonene, nonane; C10: 1-decene, decane; C11: 1-undecene, undecane; C12: 1-dodecene, dodecane; C13: 1-tridecene, tridecane; C14: 1-tetradecene, tetradecane; C15: 1-pentadecene, pentadecane; C16: 1-hexadecene, hexadecane; C17: 1-heptadecene, heptadecane; C18: 1-octadecene, octadecane; C19: 1-nonadecene, nonadecane; C20: 1-eicosene, eicosane; (*d*) Mass chromatogram (m/z 108), 1: 3-methylphenol; 2: 3-ethenylphenol, 3-ethylphenol; 3: 3-propenylphenol, 3-propylphenol; 4: 3-butenylphenol, 3-butylphenol; 5: 3-pentenylphenol, 3-pentylphenol; 6: 3-hexenylphenol, 3-hexylphenol; 7: 3-heptenylphenol, 3-heptylphenol; 8: 3-octenylphenol , 3-octylphenol; 9: 3-nonenylphenol, 3-nonylphenol; 10: 3-decenylphenol 3-decylphenol; 11: 3-undecenylphenol, 3-undecylphenol; 12: 3-dodecenylphenol, 3-dodecylphenol; 13: 3-tridecenylphenol, 3-tridecylphenol; 14: 3-tetradecenylphenol, 3-tetradecylphenol; 15: 3-pentadecenylphenol, 3-pentadecylphenol; 16: 3-hexadecenylphenol, 3-hexadecylphenol; 17: 3-heptadecenylphenol, 3-heptadecylphenol.

Peaks 1–17 were detected in the mass chromatogram (m/z 108) as shown in Figure 8*d*. These peaks were identified as alkenylphenols and alkylphenols having C1-C17 side chains. These components were also detected at 400°C as described before. The alkenylphenols and

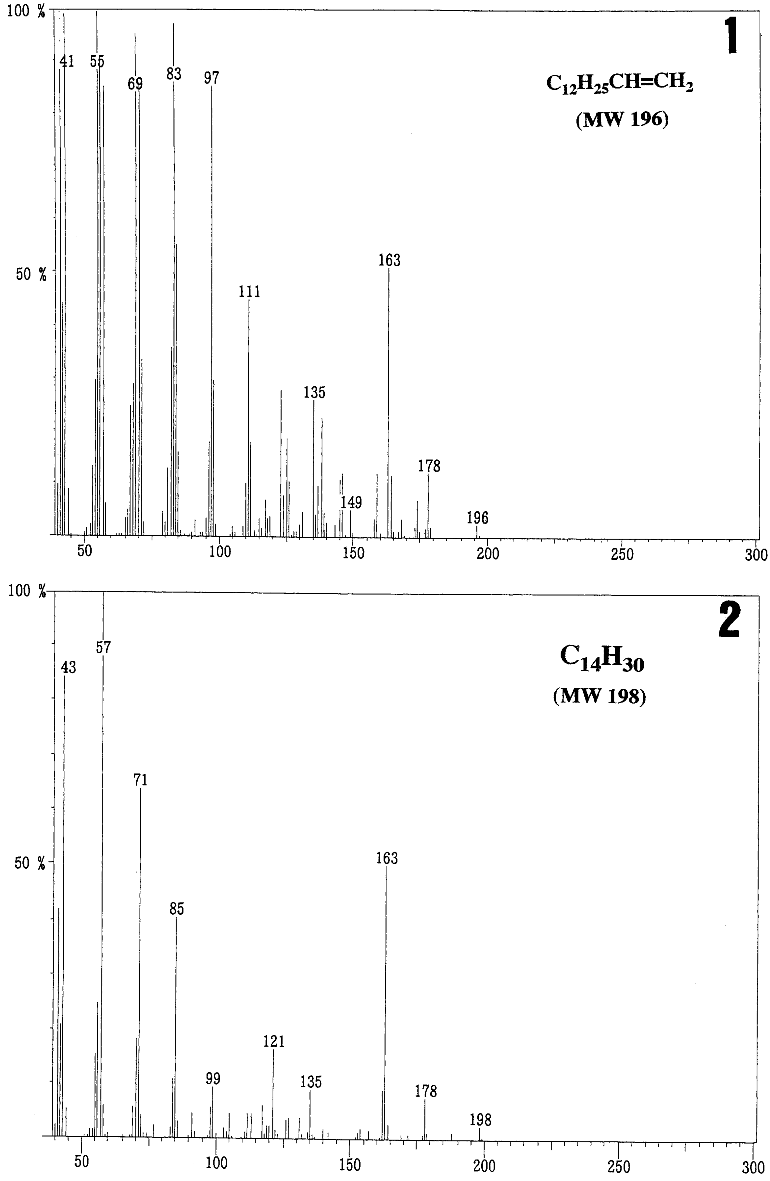
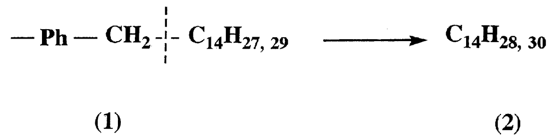


FIGURE 9 Mass spectra of peak C14. 1: 1-tetradecene; 2: tetradecane.



SCHEME 4 Pyrolysis mechanism of the terminal groups. (1) Terminal groups of the cardanol polymers; (2) 1-tetradecene, tetradecane.

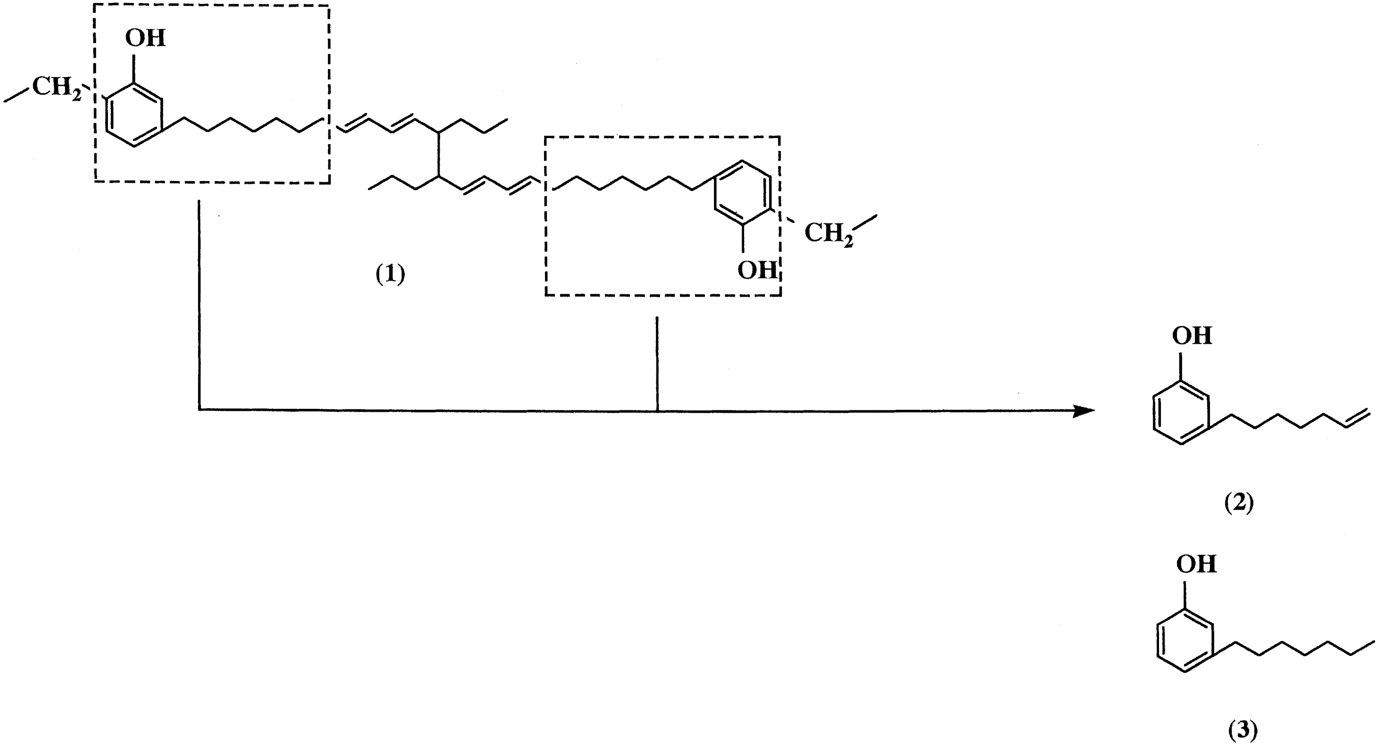
alkylphenols detected at 500°C after pyrolysis at 400°C are the products of cross-linked cardanol polymers. This was ascertained from the relative peak intensity of pentadecenylphenol and pentadecylphenol (peak 15), which is the terminal group of cardanol polymers, which is lower than that of peak 15 detected by the pyrolysis at 400°C, as shown in Figure 5.

The relative peak intensity of heptenylphenol and heptylphenol (peak 7) are highest as shown in Figure 8*d*. The cross-linked cardanol polymers mainly consist of trienyl- and dienylcardanol, because these components are more active during polymerization. In addition, the double bonds of these olefin side chains are located at the 8th carbon[28]. It was reported, however, that the α- and β-positions to the double bonds of the olefin are most susceptible to thermal cleavage[29]. Therefore, the highest yield of heptenylphenol and heptylphenol (peak 7) can be attributed to the preferential cleavage at the α–position to the 8th-double bonds of trienyl- and dienylcardanol polymers as shown in Scheme 5.

The results described above showed that cardols and cardanols polymerize into cashew resin by the autoxidative side-chain/side-chain C-C coupling, and the cross-linked cardanol polymers consist of more trienyl- and dienylcardanols than alkylcardanol.

CONCLUSION

The technical CNSL obtained from the raw CNSL by distillation was analyzed to investigate its constituents using GC/MS. The results showed that technical CNSL consists of cardanols and cardols but not 2-methylcardol. Hexamethylenetetramine was added to technical CNSL and the mixture was polymerized into cashew resin film by heating. The film was analyzed using two-stage Py-GC/MS and its structure was studied. It was found that the cashew resin is terminated with saturated cardols and cardanols by pyrolysis at 400°C. The results are effective for distinguishing cashew resin from other resins and saps. Furthermore, the



SCHEME 5 Pyrolysis mechanisms of cardanol polymer. (1) Side-chain/side-chain C-C coupling polymer of cardanol; (2) 3-heptenylphenol; (3) 3-heptylphenol.

pyrolysis at 500°C revealed that the autoxidative side-chain/side-chain C-C coupling accelerated the cross-linking of trienyl- and dienylcardanols during the polymerization.

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