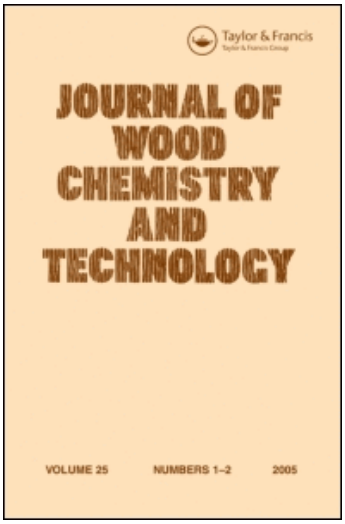

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EXTRACTION AND CHARACTERIZATION OF LIPOPHILIC EXTRACTIVES FROM RICE STRAW. II. SPECTROSCOPIC AND THERMAL ANALYSIS

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ABSTRACT

Five lipophilic extractives isolated with toluene–ethanol (2 : 1, v/v), chloroform, petroleum ether, dichloromethane, and hexane from rice straw were examined by Fourier transform infrared, ^{1}H and ^{13}C nuclear magnetic resonance spectroscopies, and thermal analysis. In comparison with other four extractives, the extractives, isolated with toluene–ethanol (2 : 1, v/v), showed much lower absorption bands at 2926 and 2853, and 1739 and 1713 cm^{-1} for CH_2 and CH_3 stretching

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frequencies, and C=O stretching in ester and acids, indicating a much lower content of the lipophilic substances in the extractives. A rather weak band at 1030 cm^{-1} in the extracts, isolated with petroleum ether and dichloromethane, indicated that the two extracts were relatively free of co-extracted polysaccharides. The thermal analysis showed that the melting temperatures of the extractives occurred between 57.1 and 71.4°C, indicating a mixture of the extracts.

Key Words: Rice straw; Lipophilic extractives; FT-IR; 1H and 13C-NMR; Thermal analysis

INTRODUCTION

Classical methods for quantitatively analyzing extractives require many steps, including solvent extraction, saponification, separation of the acid and neutral fractions, and analysis of the derivatized acids by gas chromatography (GC). This technique can separate the lipid complex into resin acids, free and combined fatty acids, and non-saponifiables.[1–3] A number of other techniques, such as thin layer chromatography,[4] high performance liquid chromatography (HPLC),[5] and high performance size exclusion chromatography,[6] for analysis of extractives in wood samples have been developed. However, most methods are too laborious for analysis of a large number of samples.

In recent years, Fourier transform infrared (FTIR) spectroscopy has received great attention in quantitative analysis of wood resin and contaminants in pulp and pitch deposit extractives.[7] It is an extremely powerful analytical technique for both qualitative and quantitative studies of structural properties of the extractives. Furthermore, FTIR is non-destructive and often permits a sample to be analysed in situ. The region between 800 and 2500 cm^{-1} has been shown to have potential applications in the pulp and paper industry. It has been used in determining wood resin directly on ground wood pulp.[1] Similarly, carbon-13 nuclear magnetic resonance (NMR) spectroscopy is also a useful tool in the study of various problems related to lipid technology. Complementary and/or confirmatory information regarding the lipid class composition and the total acyl profile, particularly for an overall view of the lipid structure, can be inferred simultaneously from the same ^{13}C NMR spectrum.[8] This technique enables quantification of the extractives in terms of total fatty acids, resin acids, triglycerides, and fatty acid esters.

The first paper of this series reported studies of chemical composition of the five extractives isolated from rice straw based on gas chromatography using a medium-length high temperature capillary column with a thin film.[9] In this continuing study, the five preparations of the lipophilic extractives were further investigated by spectroscopic techniques such as Fourier transform infrared, and ^{1}H and ^{13}C nuclear magnetic resonance as well as thermal analysis, and the results are reported.

RESULTS AND DISCUSSION

FTIR Spectra

FTIR spectroscopy has received great attention in quantitative analysis of lipids over the years. It has a major advantage over the conventional grating instruments, having more energy throughput, excellent reproduc-

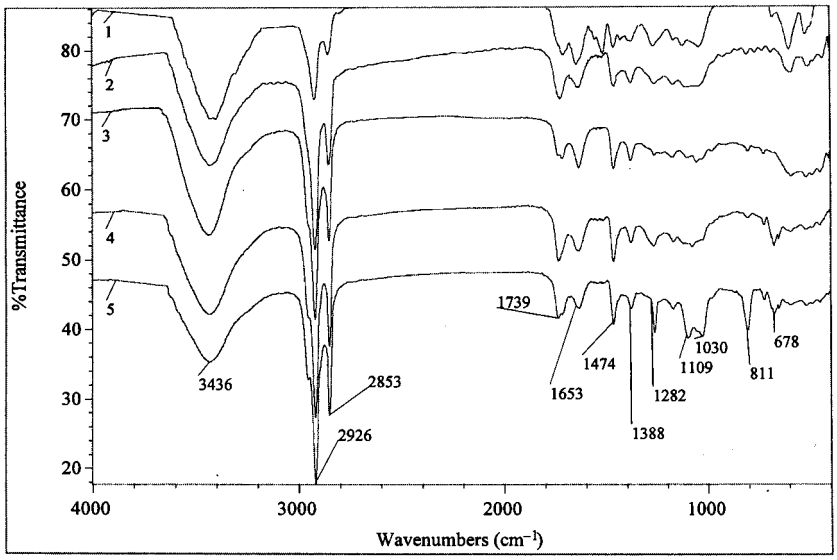

Figure 1. FTIR spectra of extractives obtained by extraction from rice straw with toluene–ethanol (2/1, v/v, spectrum 1), chloroform (spectrum 2), petroleum ether (spectrum 3), dichloromethane (spectrum 4), and hexane (spectrum 5) for 12 h in a Soxhlet.

ibility, and accuracy from the laser source.[7] Figure 1 illustrates the FTIR spectra of toluene–ethanol extract (spectrum 1), chloroform extract (spectrum 2), petroleum ether extract (spectrum 3), dichloromethane extract (spectrum 4), and hexane extract (spectrum 5). In comparison with the other four spectra, spectrum 1 showed much lower absorption bands at 2926 and 2853, and 1739 and 1713 (data not shown) cm^{-1} for CH_2 and CH_3 stretching frequencies, and C=O stretching in ester and acids, indicating a much lower content of the lipophilic substances in the extractives. Conversely, as can be seen from Figure 1, rather similar strong absorbances of these bands in the spectra of F2, F3, F4, and F5 implied a similar structure of the four extractives, which enriched in lipophilic extractives. This observation corresponded to the results obtained by GC analyses. In addition, occurrence of two small bands at 1513 and 1426 cm^{-1} in F1 is undoubtedly due to the presence of small amounts of co-extracted phenolic compounds in toluene–ethanol extract, which also supported the results obtained by HPLC analyses.[9]

A prominent peak at 3436 cm^{-1} is attributed to the OH stretching vibration in sterols, mono- and diglycerides or co-extracted polysaccharides, or water in samples.[10] Two strong bands at 2926 and 2853 cm^{-1} arise from methylene and methyl stretching frequencies, respectively. The carbonyl bonds in esters (waxes, sterol esters, triglycerides) are produced at 1739 cm^{-1}, whereas the carbonyl bonds in free fatty and resin acids give a band at 1713 cm^{-1} in F3 and F5 spectra, and as a shoulder in F1, F2, and F4 extracts and strongly overlapped with the previous one. The C=C cis stretching (in unsaturated fatty acids and their esters or in sterols and steryl esters) exhibits a strong absorption band at 1653 cm^{-1}. Two bands at 1474 and 1388 cm^{-1} are assigned to the methylene bending vibration and methyl symmetrical bending vibration, respectively. The carbon single bonded oxygen (C-O) or bonded hydroxyl (C-OH) in carboxylic acids, bending or stretching vibration gives a absorption band at 1282 cm^{-1}.[11] The weak broad band at 1175 cm^{-1} (data not shown) corresponds to the C-O stretching in the aliphatic esters (O=C-O-$CHCH_2$-). In the region (1200–950 cm^{-1}) of polysaccharides,[12] two absorption bands at 1109 and 1030 cm^{-1} are attributed to the C-O or C-C stretching and the ether bond (C-O-C) symmetrical stretching in co-extracted polysaccharides, respectively. This is particularly true in toluene–ethanol extract (F1), chloroform extract (F2), and hexane extract (F5). These observations, in general, confirmed the results obtained by GC analyses, which found that the extracts of toluene–ethanol extract (F1), chloroform extract (F2), and hexane extract (F5) contained 42.56, 37.68 and 27.61% of unidentified compounds such as co-extracted polysaccharides, ash or salts, respectively, except for azelaic and maleic acids and phenolic compounds.

^{1}H and ^{13}C NMR Spectra

NMR spectroscopy is another non-destructive method for structural characterization of lipophilic substances. To further characterize the dichloromethane extract, an ^{1}H NMR study was carried out and its spectrum is shown in Figure 2. In addition to the most intense signal at 1.28 ppm for the methylene aliphatic protons and a very strong signal at 0.88 ppm for methyl protons, the spectrum exhibits peaks at ~2.0 ppm for protons on carbons adjacent to carbonyl in esters (CH_2-C=O), ~2.3 ppm for protons on carbons adjacent to an carboxylic acid group ($C\underline{H}_2$-COOH), ~4.2 ppm for protons on carbons adjacent to alcohols (C<u>H</u>OH) or ethers (C<u>H</u>-O-C), and 5.1–5.5 ppm for protons on carbons adjacent to alkene (C=C<u>H</u>).[13] These observations were in good agreement with the findings of functional groups in the extract identified by FTIR. Note that the three peaks between 7.2 and 7.8 ppm are presumed to be due to the residual chloroform present in $CDCl_3$ and should be ignored.

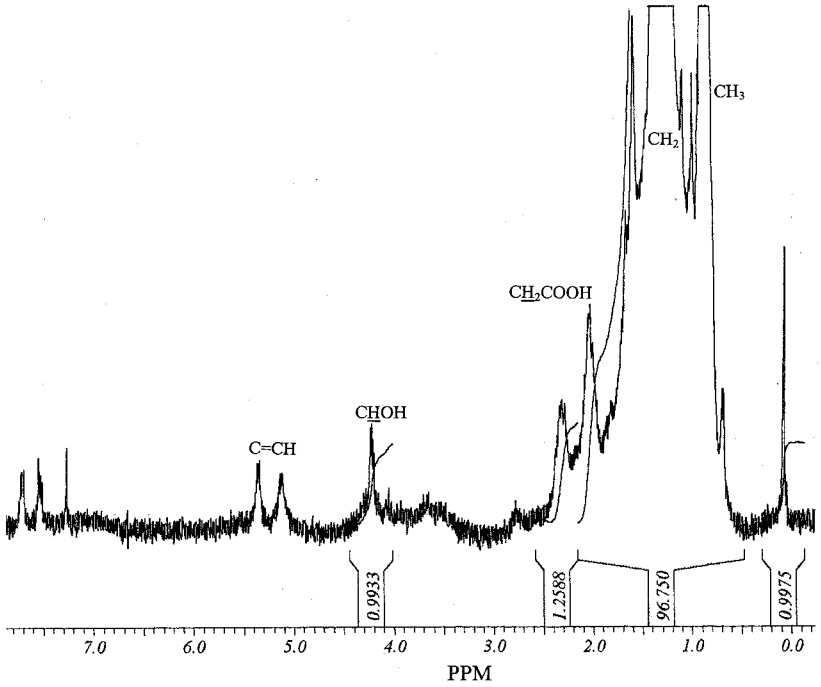

Figure 2. ^{1}H NMR spectrum of dichloromethane extract (F4).

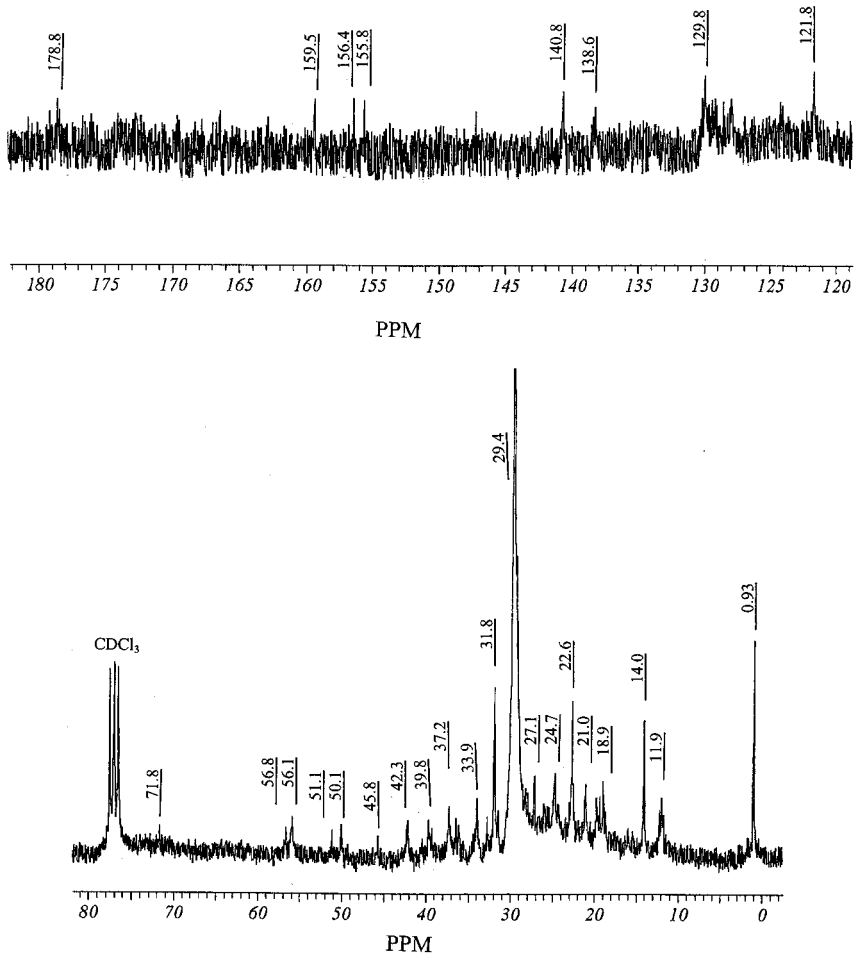

Figure 3. The ^{13}C NMR spectrum of hexane extract (F5).

A solution state ^{13}C NMR spectrum of hexane extract of rice straw (Figure 3) shows the great complexity of the mixture. However, the carbon atoms from unsaturated compounds (110–160 ppm), aliphatic (0–34 ppm) and C-O substituted (40–90 ppm) structures, and functional groups (170–200 ppm) were clearly distinguished from each other. The signal at 178.8 ppm is indicative of carbonyl groups in free fatty acids. The carbonyl groups of fatty acid esters occur as a weak broad peak at 173–174 ppm (data not shown).[14] The signals at 159.5, 156.4, 155.8, 140.8, 138.6, and 121.8 ppm are originated from unsaturated carbon (>C=) in resin acids,

sterols or steryl esters, and signals at 129.8 and 128.2 ppm (data not shown) are attributed to unsaturated carbon double bond (-CH=CH-) in fatty acids or fatty acid esters. The carbon bonded oxygen group (>C-O) in sterol or steryl esters gives signals at 71.8, 56.8, 56.1, 51.1, 50.1, 45.8, and 42.3 ppm.[8] The peak at 14.0 ppm arises from the methyl end of the chain, whereas the strongest signal at 29.4 ppm, together with the signals at 18.9, 21.0, 22.6, 24.7, 27.1, 31.8, and 33.9 ppm, originate from methylene units successively further from the methyl group.[13] Two peaks at 37.2 and 39.8 ppm are probably due to the methine group in resin acids, sterols or steryl esters.

Thermal Analysis

To further study the thermal stability and the melting temperature of the lipophilic extractives, thermal analysis of the petroleum ether extract was carried out using thermogravimetric analysis and differential scanning calorimetry, and their curves are illustrated in Figure 4. As Figure 4 shows, the maximum rate of weight loss can be observed between 310 and 440°C, and its decomposition temperature started at 186°C. The decomposition temperature at 10% weight loss occurred at 252°C. When the temperature rose to 400°C the weight loss increased significantly to over 60%. Non-volatile residues at 600°C were small, ~14% of the total extractives, and

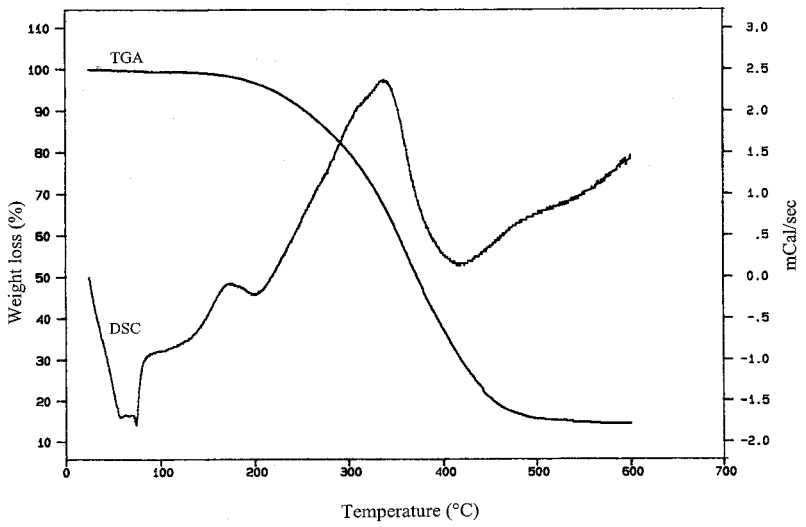

Figure 4. Thermograms of petroleum ether extract (F3).

are probably due to the contaminates, such as ash and salts from rice straw. The melting temperatures, as shown in the differential scanning calorimetry (DSC) curve, occurred between 57.1 and 71.4°C, indicating a mixture of the extract. This figure is typical of results found for all of the wood resins tested, in which the melting points appeared temperature range between 30 and 70°C.[15]

EXPERIMENTAL

Material

Rice straw was obtained from the experimental farm of the North-Western Science and Technology University of Agricultural and Forestry (Yangling, P. R. China). It was dried in sunlight and then cut into small pieces. The cut straw was ground to pass a 2.5 mm size screen. The detailed isolation procedure of the five lipophilic extractives and the method for separation of their components by gas chromatography were reported in a previous paper of this series.[9]

FTIR and ^{1}H and ^{13}C NMR Spectroscopies

FTIR spectra were obtained on an FTIR spectrophotometer (Nicolet 510) using a KBr disc containing 1% finely ground samples. The solution-state ^{1}H and ^{13}C NMR spectra were obtained on a Bruker MSL-300 spectrometer at 300 and 74.5 MHz in deuteriochloroform, respectively. An ^{1}H NMR spectrum was recorded at 25°C from 15 mg of sample dissolved in 1.0 ml deuteriochloroform for a total of 32 scans using an 8 μs (~90°C) pulse and a 4 s delay time between scans. A solution ^{13}C NMR spectrum was recorded at 25°C from 80 mg of sample dissolved in 1.0 ml chloroform-d after 3000 scans. A 70° pulse flipping angle, a 10 μs pulse width and a 15 s delay time between scans were used.

Thermal Analysis

Thermogravimetric analysis (TGA) and DSC of the extractives were performed with a simultaneous thermal analyzer (NETZSCH STA-409). The apparatus was continually flushed with nitrogen. The sample weighed between 8 and 15 mg. Each sample was heated from room temperature to 600°C at a rate of 10°C per minute.

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