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Composition of acidic components in Chinese raw tall oil

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Abstract Chinese raw tall oil samples, which were obtained from pulp and papermaking factories in Qingzhou and Jiamusi, were first divided into acidic and neutral parts with a diethylaminoethyl-Sephadex (DEAE-Sephadex) gel column. The acidic components were then analyzed qualitatively and quantitatively by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). The results obtained are as follows: Most of the compounds that comprised 0.1% or more of the components were identified. Secodehydroabietic, 8,15-pimaradienoic, 8,15-isopimaradienoic, 7,13,15-abietatrien-18-oic acid, and others were found for the first time in Chinese tall oil; they have not been found in Chinese fatty rosin. Docosan-1,22-dioic acid was also found in tall oil for the first time.

Key words Tall oil · Resin acid · Fatty acid

Introduction

Raw tall oil, a by-product of sulfate (kraft) pulping of conifer wood chips, is a semisolid material. It is obtained by concentrating the black-colored liquor, followed by salting out a semisolid soap, which is skimmed off and acidified with sulfuric acid or hydrochloric acid. Tall oil is a complex mixture containing fatty acids, resin acids, and neutral substances.^{1,2} In most developed Western countries, tall oil is an important domestic source of rosin and a major contributor to the production of industrial fatty acids. For example, in

1985 in the United States the yield of tall oil rosin (TOR) was about 2 million tons, 70% of the total yield of rosin.³ That same year, the yield of tall oil fatty acids (TOFAs) was 295 000 tons, 36.4% of the total yield of fatty acids. Compared with that of the developed Western countries, the yield of tall oil in China is small. The annual output of raw tall oil is currently less than 15 000 tons. The reason is that the main raw materials used for pulping in most pulp and papermaking factories are rice straw and wheat grass. Only in Qingzhou, Nanping, and Jiamusi do a few factories use wood as the main raw materials.

Because of the small output of tall oil, studies of tall oil are not considered important in China. There are no reports of detailed compositional analysis of Chinese tall oil. The main object of this study was to characterize the raw tall oil produced in southern and northern China and to identify the principal components of the contained acidic materials.

Because raw tall oil contains more than 80 compounds,⁴⁻⁸ prefractionation of acids from neutral materials is a prerequisite for analyzing a complex mixture of tall oil. In the study reported here, we separated the acidic fraction from tall oil using diethylaminoethyl-Sephadex (DEAE-Sephadex) followed by analysis with gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) after methylation; we identified diterpenoic acids of pimarane and abietane types and fatty acids. The qualitative and quantitative compositions of tall oils produced in southern and northern China are presented herein.

Experimental procedures

Material

The raw tall oil samples A and B were obtained from the pulp and papermaking factories of Qingzhou and Jiamusi (China). The fatty rosin sample C was obtained from Rosin Factory of Youxi in Fujian (China). The composition of acidic components in fatty rosin sample C has been analyzed and reported elsewhere.⁹

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Separation of acidic fraction from neutrals in raw tall oil

Raw tall oil (0.6g) was subjected to a DEAE-Sephadex A-25 (OH form) column (30×1 cm i.d.) in a mixed solvent of diethylether-methanol-water (90:9:1, v/v). The column was first eluted with a mixed solvent of diethylether-methanol-water (400 ml) at a flow rate of 4 ml/min to afford the neutral fraction. Acidic components were then eluted with 400 ml of the mixed solvent containing 3.6g formic acid.

The bulk of the solvent from both the neutral and acidic fractions was removed on a rotary film evaporator. The remaining solvent and formic acid in the acidic fraction were removed carefully by heating on a steam bath under a stream of N_2 , followed by drying under reduced pressure at $40^\circ C$.

The concentrate of each acidic fraction was dissolved in mixed solvent of diethylether-methanol (9:1, v/v), and a known amount of heptadecanoic acid was then added as an

Table 1. Gross compositional characteristics of Chinese raw tall oil

Raw tall oil samples	Composition (%)			
	DEAE-Sephadex separation		Acids	
	Neutrals	Acids	Fatty acids	Resin acids
A	11.33	78.51	49.96	50.04
B	35.00	58.43	46.46	53.54

A, raw tall oil sample obtained from pulp and papermaking factory of Qinzhou in Fujian, China; B, raw tall oil sample obtained from pulp and papermaking factory of Jiamusi in Heilongjiang, China

Results are given in percent composition

Table 2. Gas chromatography-mass spectrometry analysis of acidic fraction

Tall oil acids of sample A			Tall oil acids of sample B		
Peak no.	Compounds (acid as methylester)	%	Peak no.	Compounds (acid as methylester)	%
1	Contaminant		1	Cembrene	1.02
2	Contaminant		2	Palmitic	1.08
3	Tetradecanoic	Trace	3	Contaminant	
4	Palmitoleic	Trace	4	Contaminant	
5	Palmitic	0.82	5	14-Methylhexadecanoic	0.64
6	Contaminant		6	Heptadecanoic (internal standard)	
7	14-Methylhexadecanoic	0.14	7	Pinolenic	2.78
8	Heptadecanoic (internal standard)		8	5,9-Octadecadienoic	
9	Unknown	Trace	9	Linoleic	5.26
10	Pinolenic	0.20	10	Oleic	
11	Oleic	10.09	11	Stearic	3.67
12	Stearic	0.60	12	9c, 11t-Octadecadienoic	1.09
13	Octadecadienoic (9t,11t or 10t,12t?)	0.40	13	10t, 12c-Octadecadienoic	1.28
14	Secodehydroabietic	0.29	14	Octadecadienoic (9t, 11t, or 10t, 12t?)	0.92
15	8,11-Octadecadienoic	0.57	15	8,15-Isopimaradien-18-oic	1.56
16	Pimaric	3.97	16	Isopimaradien-3-one	Trace
17	Sandaracopimaric	0.72	17	Pimaric	Trace
18	Eicosatrienoic (5,11,14 or 7,11,14?)	0.73	18	Sandaracopimaric	2.06
19	Isopimaric	1.33	19	Dehydroabietal	0.86
20	8,15-Pimaradienoic and palustric	3.33	20	Eicosatrienoic (5,11,14 or 7,11,14?)	0.66
21	Dehydroabietic	5.19	21	Isopimaric	10.64
22	Abietic	20.40	22	8,15-Pimaradienoic and palustric	13.85
23	Neoabietic	2.32	23	Daniellic	2.49
24	8,13(15)-Abietadien-18-oic	Trace	24	Dehydroabietic	5.58
25	Unknown	1.17	25	Abietic	10.86
26	7,13,15-Abietatrien-18-oic	0.36	26	Contaminant	
27	Retinoic	10.79	27	Neoabietic	5.16
28	Docosanoic	35.08	28	7,13,15-Abietatrien-18-oic	0.77
29	2 α ,3 β ,5 α -Aspidofractinine-3-methanol	0.64	29	Retinoic	1.12
30	Unknown	0.27	30	Docosanoic	25.47
31	Tetracosanoic	0.31	31	2 α ,3 β ,5 α -Aspidofractinine-3-methanol	0.49
32	Unknown	Trace	32	Unknown	Trace
33	Docosan-1,22-dioic	Trace	33	Tetracosanoic	0.46

A, raw tall oil sample obtained from pulp and papermaking factory of Qinzhou in Fujian, China; B, raw tall oil sample obtained from pulp and papermaking factory of Jiamusi in Heilongjiang, China

?, position of the double bond is not certain

The configuration of double bond and overlapped peak was identified by comparing their relative retention time with those of standard samples

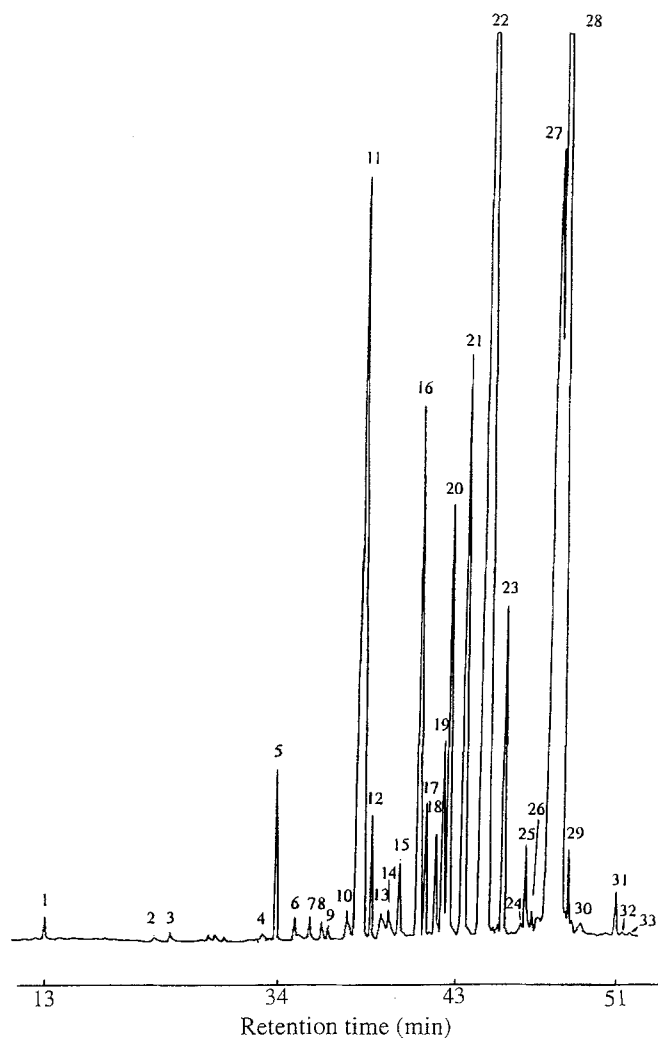


Fig. 1. Chromatogram of the acid fraction of sample A. Peak numbers in the figure are shown in Table 2

internal standard. The acidic compounds were methylated with diazomethane prepared by the reaction of *N*-methyl-*N*-nitroso-paramethylbenzulfamide with an aqueous solution of potassium hydroxide. After removing diazomethane, the resultant solution was used for GC and GC-MS analyses.

GC analysis of the acidic fractions

A Shimadzu GC-8A gas chromatograph equipped with a hydrogen flame ionization detector (FID) was used for analyzing the acidic fractions. Separation was conducted on a DB-5 glass capillary column (30m × 0.25mm i.d.). The operating conditions of the column were as follows: inlet temperature 280°C, nitrogen carrier gas at a flow rate of 5ml/min, and temperature elevated from 60°C to 260°C, increasing at a rate of 4°C/min.

GC-MS analysis of the acidic fractions

The components of the acid fractions were identified on a Shimadzu JM3-D300 GC-MS system. A GC equipped with

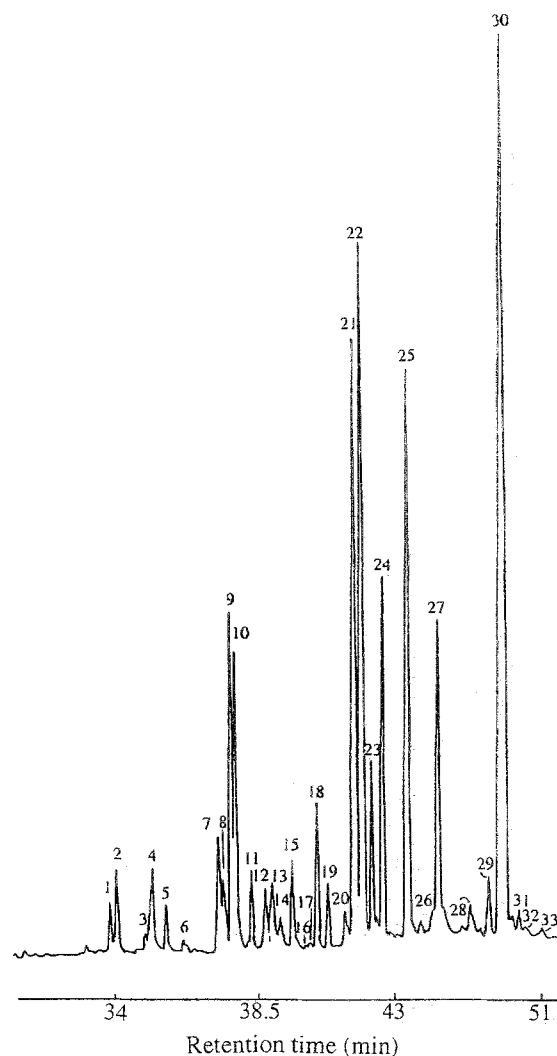


Fig. 2. Chromatogram of the acid fraction of sample B. Peak numbers in the figure are shown in Table 2

a DB-5 glass capillary column (30m × 0.25mm i.d.) was connected directly to the mass spectrometer. The analytical conditions for GC were the same as stated above, except helium was used as a carrier gas at a flow rate of 1ml/min. The operating conditions of the mass spectrometer were as follows: ionization voltage 70eV, accelerating voltage 3kV, ionization current 300μA, and temperature of ionization source 285°C.

Identification of the peaks was based primarily on the mass spectra by comparing them with published MS spectra data.^{10,11} Some peaks were identified by comparing their relative retention time and MS data with those of standard samples.

Results and discussion

The few pulp and papermaking factories that use pine wood as the main raw material in China are mostly located in

Table 3. Composition of resin and fatty acids in Chinese raw tall oils

Compounds	Acid composition of various raw tall oil samples ^a	
	Sample A	Sample B
Resin acids		
Secodehydroabietic	0.29	—
Pimaric	3.97	Trace
Sandaracopimaric	0.72	2.06
Isopimaric	1.33	10.64
8,15-Isopimaradienoic	—	0.78
8,15-Pimaradienoic	3.33	13.85
Palustric		
Dehydroabietic	5.19	5.58
Abietic	20.40	10.86
8,13(15)-Abietadien-18-oic	Trace	—
Neoabietic	2.32	5.16
7,13,15-Abietatrien-18-oic	0.36	0.77
Retinoic	10.79	1.12
Total resin acids	48.70	50.82
Fatty acids		
Tetradecanoic (14:0)	Trace	—
Palmitoleic (16:1)	Trace	—
Palmitic (16:0)	0.82	1.08
14-Methylhexadecanoic (17:0)	0.14	0.64
Pinolenic (18:3)	0.20	2.78
5,9-Octadecadienoic (18:2)	—	
Linoleic (18:2)	—	5.26
Oleic (18:1)	10.09	
Stearic (18:0)	0.60	3.67
Octadecadienoic (18:2) (9t,11t, or 10t,12t?)	0.40	0.92
8,11-Octadecadienoic (18:2)	0.57	0.78
9c,11t-Octadecadienoic (18:2)	—	1.09
10t,12c-Octadecadienoic (18:2)	—	1.28
Eicosatrienoic (20:3) (5,11,14 or 7,11,14?)	0.73	0.66
Docosanoic (22:0)	35.08	25.47
Tetracosanoic (24:0)	0.31	0.46
Docosan-1,22-dioic (22:0)	Trace	—
Total fatty acids	48.94	44.09

^a Percent of the total acids. A, raw tall oil sample obtained from pulp and papermaking factory of Qinzhou in Fujian, China; B, tall oil sample obtained from pulp and papermaking factory of Jiamusi in Heilongjiang, China

?, position of the double bond is not certain

The configuration of double bond and overlapped peak was identified by comparing their relative retention time with those of standard samples

Fujian and Heilongjiang provinces. The pine trees in southern China are mainly masson pine (*Pinus massoniana*), and the trees in northern China are mainly larch (*Larix gmelini*) and Korean pine (*Pinus koraiensis*). The samples from Qingzhou and Jiamusi are thought to be representative of Chinese tall oil.

The general characteristics of Chinese raw tall oil are summarized in Table 1. The content of neutral substances and acids was determined by the DEAE-Sephadex method. It was found that the content of neutrals in sample A was much lower than in sample B, and that in both samples the content of resin acids was somewhat higher than that of fatty acids.

The results obtained by GC and GC-MS analyses of the acid fractions of samples A and B are shown in Figs 1 and 2 and Table 2. The main resin and fatty acids are listed in Table 3. Preliminary analyses of samples A and B showed that resin acids of the tricyclic abietane and pimarane types accounted

for most of the components of the total resin acids, and 18- and 22-carbon fatty acids accounted for most of the total fatty acids. Most of the fatty acids were monoacids.

We compared the results of GC and GC-MS analyses; and the differences between the acidic components of raw tall oils obtained from different places are shown in Table 3. We found that the resin acids 8,13(15)-abietadien-18-oic acid and secodehydroabietic acid, which had not previously been found in Chinese tall oil, were present in sample A, but in small amounts (less than 0.5%). Also, 8,15-isopimaradienoic acid was found in sample B.

There were differences between samples A and B for the fatty acids. 14-Carbon and 16-carbon monoacids were present in sample A; but linoleic acid and 5,9-, 9,11-, and 10,12-octadecadienoic acids were not found in this sample. In addition, a 22-carbon diacid was present in sample A at a very low level. These differences between samples A and B might be due to the use of different wood species and differ-

Table 4. Main resin acids in tall oil acid fraction and in fatty rosin obtained from China

Acid type	Main resin acids and the contents of various samples (%) ^a	
	A	C ^b
Pimaric	8.15	9.15
Sandaracopimaric	1.48	3.20
Isopimaric	2.73	3.56
8,15-Pimaradienoic	6.84	—
Palustric		22.09
7,13,15-Abietatrien-18-oic	0.74	—
Dehydroabietic	10.66	6.00
Abietic	41.89	41.80
Retinoic	22.16	—
Neoabietic	4.76	14.17

^aPercent of the total resin acids. A, raw tall oil sample obtained from pulp and papermaking factory of Qingzhou in Fujian, China; C, fatty rosin obtained from Youxi in Fujian, China

^bThe data for sample C are from Chang et al.⁹

ent pulping conditions. In southern China masson pine is the major tree used for pulping, whereas in northern China larch and Korean pine are the major trees.

The various components of resin acids found in tall oil and fatty rosin are compared in Table 4. Tall oil sample A and fatty rosin sample C were obtained from the same area and the same type of pine (masson pine). Even so, there was a small difference in the resin acid components for the two samples. The amounts of pimarane type resin acids were almost equivalent for samples A and C, but the amounts of abietane type resin acids were different. Palustric acid and neoabietic acid were present in tall oil in obviously small amounts, and dehydroabietic acid was slightly abundant; only the amount of abietic acid hardly varied. In addition, resin acids such as 8,15-pimaradienoic acid, 7,13,15-abietatrien-18-oic acid, retinoic acid (C₂₀H₂₈O₂), secodehydroabietic acid, and others were found in sample A. These resin acids might be derived from neoabietic acid, palustric acid, sandaracopimaric acid, and others during the process of pulping wood chips and acidification of tall oil soap.

Conclusions

The main compounds in the acid fractions of the raw tall oil samples A and B were identified as shown in Table 2. It was

found that ion-exchange chromatography was an efficient method for separating acids from neutrals in tall oil. The obtained acids contained little neutrals.

Tall oils from different areas had different compositions. The content of neutrals in sample A was much less than that in sample B. In the acid fractions resin acids accounted for about 50% of the content.

Secodehydroabietic acid, 8,15-pimaradienoic acid, 8,15-isopimaradienoic acid, 7,13,15-abietatrien-18-oic acid, and others were found for the first time in Chinese tall oil. They were not found in the fatty rosin. All of these acids might be artifacts derived from cooking wood chips and acidifying tall oil soap. In addition, docosan-1,22-dioic acid, which was present in sample A, was found in tall oil for the first time.

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