

NOTE

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Composition of neutral fractions in Chinese raw tall oil

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Abstract Chinese tall oil samples, obtained from pulp and papermaking factories in Qinzhou and Jiamusi of China, were first divided into acidic and neutral fractions by saponification, extraction, and distillation. The obtained neutral fractions were then analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) after silylation with bis-(trimethylsilyl) trifluoroacetamide. The results obtained show that 10 types of compound (monoterpenes, sesquiterpenes, diterpenes, triterpenes, resin alcohols, resin aldehydes, steroids, fatty alcohols, phenols, stilbenes) exist in the neutral fractions of Chinese raw tall oil. In the neutral fractions from Qinzhou, 55 components were identified, 35 of which were found for the first time in Chinese raw tall oil; 12 components were discovered for the first time in raw tall oil. In the neutral fraction from Jiamusi, 45 components were identified, 9 of which were discovered for the first time in Chinese raw tall oil.

Key words Tall oil · Steroids · Fatty alcohols · Resin alcohols · Terpenes

Introduction

The neutral fraction of raw tall oil is a complex mixture that consists mainly of resin alcohols, resin aldehydes, phytosterols, diterpenes, and fatty alcohols.^{1–3} It is the main composition of the head fraction (fraction collected before rosin and fatty acid) and tall oil pitch (residue of raw tall oil distillation) during the distillation process of raw tall oil. For example, the head fraction and tall oil pitch contained about

25%–60% and 20%–35% neutral fraction, respectively. In addition, the existence of the neutral fraction significantly influences tall oil distillation and the utilization of distilled products such as tall oil rosin and tall oil fatty acid.

This might be the reason that the output of tall oil was small, and studies on the composition and utilization of tall oil were not regarded as important in China. There were no reports on the detailed compositional analysis of tall oil neutral fraction except for those of Jin Qi and Liu Zhiqun, who studied the composition of the neutral fraction of tall oil soap obtained in Jiamusi.⁴ They identified only a few hydroxyl group-containing components, and most of the components were not yet identified. Furthermore, there were no reports about the composition of neutral fractions obtained from tall oil produced in southern China.

The output of tall oil is increasing concomitant with the development of wood pulping. Hence, it is necessary to carry out research on the composition of tall oil to tap the wide application market of tall oil and to establish processes for its utilization. The main purpose of this study was to analyze and identify the principal components contained in tall oil neutral fractions produced in southern and northern China.

Experimental procedures

Materials and agents

Raw tall oil samples A and B were obtained from the pulp and papermaking factories of Qinzhou and Jiamusi (China), respectively. Bis-(trimethylsilyl) trifluoroacetamide (BSTFA), a silylation agent, was chromatographic grade (E. Merck, Darmstadt, Switzerland). The other agents were all analytically pure.

Extraction of tall oil neutral fractions from raw tall oil

The tall oil neutral fraction was obtained by saponifying, extracting, and distilling the raw tall oil. Raw tall oil (10g)

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was saponified with 2.7 g KOH (dissolved in a mixed solvent of 10 ml distilled water and 5 ml ethanol) at 95°C for 6 h. The reacted liquor was transferred to a separating funnel and was extracted with four 15-ml portions of ether. The combined ether layers were then washed with distilled water until neutrality was reached (tested with pH test paper). The ether layer was distilled to remove the ether totally. The residue obtained was the neutral fraction of the tall oil. The yields of tall oil neutral fractions obtained from samples A and B were 12.05% and 35.9%, respectively.

Silylation of tall oil neutral fractions

Before the gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) analyses, the neutral fraction of tall oil must first be derived because some of the components in it are hydroxyl group-containing compounds.⁵ The derivation methods are usually esterification and silylation. The silylation method is considered better for the tall oil neutral fractions because it is simple and can make the hydroxyl group-containing components completely derived. The silylation agents usually used are trime-thylchlorosilane (TMCS), hexamethyldisilazane (HMDS), *N*-(trimethylsilyl) diethylamine (TMSDMA), bis-(trimethylsilyl) acetamide, and BSTFA. BSTFA has the highest activity among them and can completely silylate the hydroxyl groups, which are a great spatial obstacle.⁶ The silylation operation was as follows.

The tall oil neutral fraction (6 mg) was dissolved in 0.5 ml trichloromethane, and the solution was injected into a capillary tube. The capillary tube was sealed after 0.05 ml of BSTFA (0.97 g/ml) was injected into it. The mixture was then left at 120°C for 4 h. The resultant solution was used for the GC and GC-MS analyses.

GC and GC-MS analyses of tall oil neutral fractions

A Shimadzu GC-9A gas chromatograph equipped with a hydrogen flame ionization detector (FID) was used for analyzing the tall oil neutrals. Separation was conducted on a DB-1 glass capillary column (30 × 0.25 mm i.d.). The operating conditions of the column were as follows: helium was used as the carrier gas at a flow rate of 1 ml/min; the split ratio was 1:10; the temperatures of the gasifying chamber and the detector were 305°C; inlet temperature was 280°C; the column temperature was elevated from 120°C (for 3 min) to 320°C (for 30 min), increasing at a rate of 4°C/min; and the injected dose of the sample was 0.3 μl.

Component identification of the neutral fraction was conducted on a Shimadzu JMS-D300 GC-MS system. The GC operating conditions were the same as stated above. The operating conditions of the mass spectrometer were as follows: electron ionization as an ion source, electron energy 70 eV, accelerating voltage 3 kV, ionization current 300 μA, scanning frequency 2 s, temperature of ionization source 210°C, scanning scope from *m/z* 40–400 to *m/z* 40–600, temperature of the joint between GC and MS 300°C, injected dose of the sample 0.25 μl.

Identification of the GC peaks was primarily based on the mass spectra by comparing them with published MS spectra data.^{7,8} Some peaks were identified by comparing their relative retention times and MS data with those of standard samples.

Results and discussion

The pulp and papermaking factories using pine wood as a main raw material in China are mostly located in Fujian and Heilongjiang. The pine trees in southern China are mainly masson pine (*Pinus massoniana* Lamb.), and in northern China they are mainly larch (*Larix gmelini* Rupr.) and Korean pine (*Pinus koraiensis* Sieb. et Zucc.). The samples from Qinzhou and Jiamusi are thought to be representative of Chinese tall oil. The contents of the neutral fractions differed in samples A and B. It was found that the neutral fraction content was much lower in sample A than in sample B.

The results of the analyses of the neutral fraction of samples A and B are shown in Figs. 1 and 2 and in Tables 1 and 2. A comparison of the compositions of samples A and B is shown in Table 3. It is seen in Table 3 that 10 kinds of neutral compound (monoterpenes, sesquiterpenes, diterpenes, triterpenes, resin alcohols, resin aldehydes, steroids, fatty alcohols, phenols, stilbenes) exist in Chinese raw tall oil; the main components were resin alcohols, steroids, and fatty alcohols. In the neutral fraction of sample A, the contents of resin alcohols, steroids, and fatty alcohols amounted to 31.2%, 32.7%, and 6.6%, respectively. In the neutral fraction of sample B, the contents of resin alcohols, steroids, and fatty alcohols amounted to 45.8%, 29.8%, and 13.8%, respectively.

Table 3 also shows that there were some differences in the components of the compounds in samples A and B. In regard to the monoterpenes, sesquiterpenes, and triterpenes, sample A contained 0.3% monoterpene-isoborneol and 3.6% sesquiterpenes, but it did not contain triterpenes. Among the sesquiterpenes, longifolene accounted for 77.8% of the total sesquiterpenes. The other sesquiterpenes, such as β -caryophyllene and 1,6-cadinadiene, were of low concentration. The types and relative contents of sesquiterpenes were similar to those in heavy turpentine oil obtained from masson pine.⁹ Monoterpenes and sesquiterpenes were not found in sample B, and the squalene content was only 0.4%.

For resin alcohols, the difference between samples A and B was also obvious. Pimarinol, sandaracopimarinol, and elliotinol were the main resin alcohols in sample A, accounting for 58.0%, 16.7%, and 9.6%, respectively, of the total resin alcohols. Larixol, neo-abietadienol, pimarinol, epimanool, and dehydroabietol were the main resin alcohols in sample B. These compounds accounted for 39.7%, 16.4%, 14.6%, 7.0%, and 7.0%, respectively, of total resin alcohol. The types and contents of resin alcohols in sample A were different from those in sample B.

Table 1. Analysis of neutral fractions from sample A

Peak no.	Compounds (alcohol as TMS ether, acid as TMS ester)	Contents (%)
1	2-Methyl phenol	0.1
2	Benzyl alcohol	0.7
3	2,6,8-Trimethylnonon-4-on-5-ene	Trace
4	<i>n</i> -Tetradecanol	0.1
5	4-Chlorophenol	0.7
6	Isoborneol	0.3
7	Diethylene glycol	Trace
8	2-(4-Methyl-3-cyclohexen)-2-propanol	0.2
9	Longipinene	0.1
10	Longicyclene	0.1
11	Unknown	0.2
12	Sativene	Trace
13	Longifolene	2.8
14	β -Caryophyllene	0.3
15	β -Farnesene	Trace
16	α -Humulene	0.1
17	Unknown	0.2
18	Contaminant	Trace
19	1,6-Cadinadiene	0.2
20	Unknown	0.8
21	Unknown (MW 292)	0.1
22	Unknown	0.2
23	Unknown	0.2
24	Unknown	0.1
25	18-Norisopimara-4(19),7,15-triene	0.2
26	Cembrene	1.6
27	Pimaradiene	0.4
28	<i>n</i> -Hexadecanol	0.3
29	Isopimaradiene	0.1
30	1,4-Dimethyl-7-isopropyl-,2,3,4,4 α ,9,10,10 α -octahydrophenanthrene	1.7
31	Androstan-4,6-diene	0.1
32	5 α -Androsta-7,9(11)-diene	0.1
33	Dehydroabietane	0.1
34	Heptadecanol	0.2
35	Hexadecanoic acid	0.2
36	Abietadiene	0.3
37	Pimarinal	2.4
38	<i>n</i> -Octadecanol	0.2
39	Isopimarinal	1.5
40	Linoleic acid	0.5
41	Oleic acid	2.9
42	Pimarinal	18.1
43	Sandaracopimarinal	5.2
44	Isopimarinal	1.2
45	Unknown	0.3
46	Unknown	0.5
47	Abietol	0.6
48	Dehydroabietol	1.0
49	Neoabietadienol	1.2
50	Elliotinol	3.0
51	Abietic acid	1.1
52	Dehydroabietic acid	1.3
53	Unknown	5.4
54	17-Methyl-5-androsten-3 β ,17 β -diol	1.7
55	5-Pregnene-3 β ,21-diol	0.3
56	5-Pregnene-3 β ,20 α -diol	0.5
57	Unknown	0.4
58	Docosanol	1.6
59	Tetracosanol	3.8
60	Hexacosanol	0.2
61	Ergosterol	0.2
62	Unknown	0.3
63	Campesterol	1.6
64	Campestanol	0.1
65	β -Sitosterol	23.1
66	β -Sitostanol	3.3
67	Cycloartenol	1.2
68	24-Methyl cycloartenol	0.2

Sample A, neutral fraction of tall oil obtained from pulp and papermaking factory of Qinzhou in China; TMS, trimethylsilane; MW, molecular weight

Table 2. Analysis of neutral fractions in sample B

Peak no.	Compounds (alcohol as TMS ether, acid as TMS ester)	Contents (%)
1	Cembrene	2.3
2	Pimaradiene	0.1
3	1-Methylene-4-methyl-7-isopropyl 1,2,3,4,4 α ,9,10,10 α -octahydrophenanthrene	0.1
4	<i>n</i> -Hexadecanol	0.2
5	Palustridiene	0.1
6	Dehydroabietane	0.2
7	Cleistantha-8,11,13-triene	0.2
8	4,4-Dimethyl-androst-1-en-3-one	1.4
9	Pimarinal	0.2
10	Palustrinol	1.0
11	Pimarinal	6.7
12	Sandaracopimarinal	Trace
13	Isopimarinal	0.4
14	Unknown (MW 360)	0.6
15	3,5-Dimethoxystilbene	0.3
16	Unknown (MW 360)	0.1
17	Linoleic acid	0.1
18	Unknown (MW 360)	0.7
19	Epimanol	3.2
20	Abietol	2.1
21	Dehydroabietol	3.2
22	Neoabietadienol	7.5
23	Elliotinol	1.9
24	Abietic acid	1.6
25	Dehydroabietic acid	Trace
26	Eicosanol	0.7
27	Larixol	18.2
28	8,13(15)-Abietadienol	0.2
29	Unknown	Trace
30	Unknown (MW 448)	1.7
31	Unknown (MW 446)	0.5
32	7,13,15-Abietatrienoic acid	0.7
33	Unknown (MW 448)	0.2
34	Unknown (MW 490)	0.2
35	Unknown	1.1
36	Unknown (MW 464)	0.9
37	17 α -Methyl-5-androsten-3 β ,17 β -diol	0.1
38	Docosanol	7.9
39	Cholesterol	0.1
40	Isomer of tricosanol	0.1
41	Unknown	0.2
42	Tricosanol	0.2
43	Tetracosanol	4.5
44	Squalene	0.4
45	1,22-Docosandiol	0.1
46	Hexacosanol	0.1
47	Contaminant	
48	Contaminant	
49	Campesterol	4.3
50	Campestanol	Trace
51	Unknown	Trace
52	β -Sitosterol	13.5
53	β -Sitostanol	2.2
54	Unknown (MW 498)	0.8
55	Parkeol	0.3
56	Lanosterol	Trace
57	Cycloartenol	4.0
58	24-Ethyl-5 α -cholest-7-ene-3 β -ol	Trace
59	Citrostadienol	1.7
60	Betulinal	1.4

Sample B, neutral fraction of tall oil obtained from pulp and papermaking factory of Jiamusi in China

Fig. 1. Chromatogram of neutral components from the tall oil produced in Qinzhou, China. *Peak numbers* in the figure are shown in Table 1

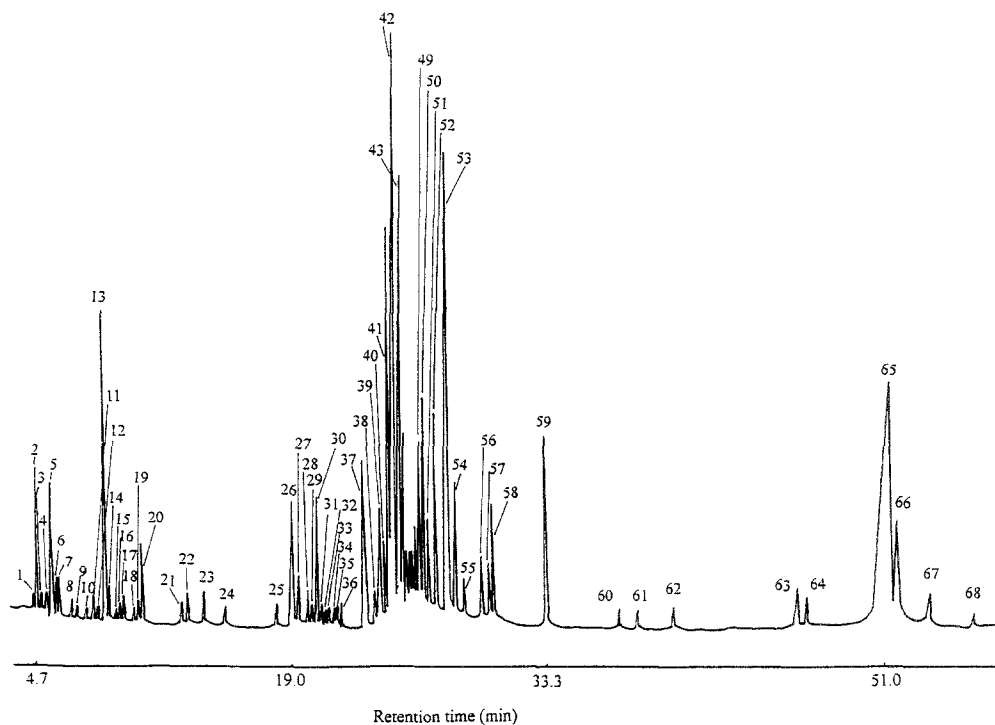


Fig. 2. Chromatogram of neutral components from the tall oil produced in Jiamusi, China. *Peak numbers* in the figure are shown in Table 2

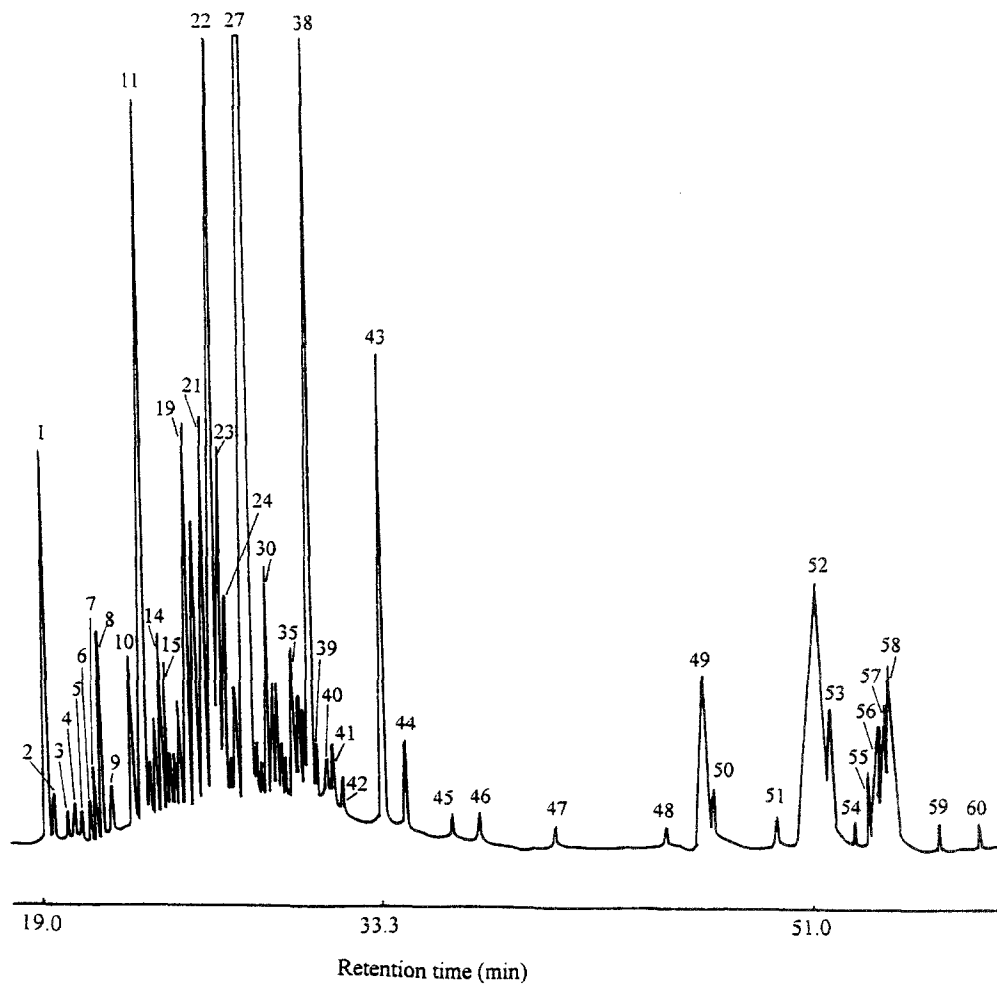


Table 3. Composition of tall oil neutral fractions obtained from southern and northern China

Compounds	Contents of components		Compounds	Contents of components	
	Sample A	Sample B		Sample A	Sample B
Monoterpenes	0.3	–	Steroids	32.7	29.8
Isoborneol	0.3	–	17 α -Methyl-5-androsten-3 β ,17 β -diol	1.7	0.1
Sesquiterpenes	3.6	–	5-Pregnene-3 β ,21-diol	0.3	–
Longipinene	0.1	–	5-Prenene-3 β ,20 α -diol	0.5	–
Longicyclene	0.1	–	Ergosterol	0.2	–
Sativene	Trace	–	Campesterol	1.6	4.3
Longifolene	2.8	–	Campestanol	0.1	Trace
β -Caryophyllene	0.3	–	β -Sitosterol	23.1	13.5
β -Farnesene	Trace	–	β -sitostanol	3.3	2.2
α -humulene	0.1	–	Cycloartenol	1.2	4.0
1,6-Cadinadiene	0.2	–	24-Methyl cycloartenol	0.2	–
Diterpenes	4.4	0.8	Cholesterol	–	0.1
18-Norisopimara-4(19),7,15-triene	0.2	–	Parkeol	–	0.3
Cembrene	1.6	0.1	Lanosterol	–	Trace
Pimaradiene	0.4	0.1	24-Ethyl-5 α -cholest-7-ene-3 β -ol	–	Trace
Isopimaradiene	0.1	–	Citrostadienol	–	1.7
Abietadiene	0.3	–	Betulinol	–	1.4
1,4-Dimethyl-7-isopropyl-1,2,3,4,4 α ,9,10,10 α -octahydrophenanthrene	1.7	–	Unknown (phytosterol)	0.3	0.8
1-Methylene-4-methyl-7-isopropyl-1,2,3,4,4 α ,9,10,10 α -octahydrophenanthrene	–	0.1	Androstan-4,6-diene	0.1	–
Dehydroabietane	0.1	0.2	5 α -Androsta-7,9(11)-diene	0.1	–
Palustridiene	–	0.1	4,4-Dimethyl-androst-1-en-3-one	–	1.4
Cleistantha-8,11,13-triene	–	0.2	Fatty alcohols	6.6	13.8
Triterpenes	–	0.4	<i>n</i> -Tetradecanol	0.1	–
Squalene	–	0.4	Diethylene glycol	Trace	–
Resin alcohols	31.2	45.8	2-(4-Methyl-3-cyclohexen)-2-propanol	0.2	–
Pimarinol	18.1	6.7	<i>n</i> -Hexadecanol	0.3	0.2
Sandaracopimarinol	5.2	Trace	<i>n</i> -heptadecanol	0.2	–
Isopimarinol	1.2	0.4	<i>n</i> -Octadecanol	0.2	–
Dehydroabietol	1.0	3.2	Eicosanol	–	0.7
Elliotienol	3.0	1.9	Docosanol	1.6	7.9
Palustrinol	–	1.0	Tetracosanol	3.8	4.5
Neoabietadienol	1.2	7.5	Hexacosanol	0.2	0.1
Abietol	0.6	2.1	Isomer of tricosanol	–	0.1
Epimanol	–	3.2	Tricosanol	–	0.2
Larixol	–	18.2	1,22-Docosandiol	–	0.1
8,13(15)-Abietadienol	–	0.2	Phenols	1.5	–
Unknown (resin alcohol, MW288)	0.4	0.6	2-Methyl phenol	0.1	–
Unknown (resin alcohol, MW288)	0.5	0.1	Benzyl alcohol	0.7	–
Unknown (resin alcohol, MW288)	–	0.7	4-Chlorophenol	0.7	–
Resin aldehydes	3.9	0.2	Stilbenes	–	0.3
Pimarinal	2.4	0.2	3,5-Dimethoxy-stilbene	–	0.3
Isopimarinal	1.5	–			

Samples A and B are neutral fractions of tall oil samples obtained from pulp and papermaking factories of Qinzhou and Jiamusi in China, respectively

The steroid content was slightly higher in the neutral fraction of sample A than in that of sample B. The main steroids were β -sitosterol, β -sitostanol, and campesterol. They accounted for 70.6%, 10.1%, and 4.9%, respectively, of the total steroids. Steroids accounted for 29.8% of the neutral fraction of sample B. Furthermore, the β -sitosterol content was slightly lower than in that of sample A. The contents of β -sitosterol, β -sitostanol, campesterol, and cycloartenol were 45.3%, 7.4%, 14.4%, and 13.4% (based on the total steroids), respectively. It was known from the analyses that sample A was more suitable for extracting β -sitosterol than sample B.

In the neutral fraction of Chinese raw tall oils, the main fatty alcohols were docosanol and tetracosanol. The types

and contents of fatty alcohols in sample A were different from those in sample B. Fatty alcohols accounted for only 6.6% of sample A. Tetracosanol had the highest content, accounting for 58.0% of the total fatty alcohols, and docosanol was the second highest (24.4% of the total fatty alcohols). In sample B, the content of docosanol was much higher than that of tetracosanol, accounting for 57.5% and 32.7% (based on the total fatty alcohols), respectively. *n*-Tetradecanol, diethylene glycol, 2-(4-methyl-3-cyclohexen)-2-propanol, *n*-heptadecanol, and *n*-octadecanol were discovered in sample A, whereas these compounds were not present in sample B. In contrast, eicosanol, tricosanol, and 1,22-docosandiol were found in sample B but not in sample A.

There were differences between samples A and B for other types of compound as well, such as the diterpenes, resin aldehydes, phenols, and stilbenes. Diterpenes, resin aldehydes, and phenols accounted for 4.4%, 3.9%, and 1.5%, respectively of sample A, but there were no stilbenes. On the other hand, the diterpene and resin aldehyde contents were much lower in sample B, accounting for only 0.8% and 0.2%, respectively. In addition, 3,5-dimethoxystilbene was found in sample B, but phenols were not.

In this study, diterpene compounds such as cembrene; 18-norisopimara-4(19),7,15-triene; 1,4-dimethyl-7-isopropyl-1,2,3,4,4 α ,9,10,10 α -octahydrophenanthrene; 1-methylene-4-methyl-7-isopropyl-1,2,3,4,4 α ,9,10,10 α -octahydrophenanthrene; and cleistantha-8,11,13-triene, which have been not reported before in tall oil, were discovered in the Chinese tall oil neutral fraction. Except for cembrene, these diterpene compounds might be derived from dehydroabietane during the process of pulping wood chips at high temperature because their chemical structures were similar to those of dehydroabietane.

The possible reason for these differences in the compounds and their contents in samples A and B might be the different sources of tall oil. In southern China masson pine is the major tree used for pulping, whereas in northern China larch and Korean pine are the major trees.

Conclusions

Most of the compounds in the neutral fractions of raw tall oil samples A and B were identified. The neutral fraction of Chinese raw tall oil consisted of 10 types of compound: monoterpenes, sesquiterpenes, diterpenes, triterpenes, resin alcohols, resin aldehydes, steroids, fatty alcohols, phenols, and stilbenes.

The neutrals fractions of raw tall oil obtained from different sources had different compositions. The main

components were resin alcohols, steroids, and fatty alcohols. Triterpenes and stilbenes were not found in sample A; and monoterpenes, sesquiterpenes, and phenols were not found in sample B.

Components such as isoborneol; longipiene; longicyclene; sativene; longifolene; β -caryophyllene; β -farnesene; α -humulene; 1,6-cadinadiene; cembrene; 18-norisopimara-4(19),7,15-triene; 1,4-dimethyl-7-isopropyl-1,2,3,4,4 α ,9,10,10 α -octahydrophenanthrene; 1-methylene-4-methyl-7-isopropyl-1,2,3,4,4 α ,9,10,10 α -octahydrophenanthrene; cleistantha-8,11,13-triene; and 1,22-docosandiol were found for the first time in the neutral fraction of raw tall oil.

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