Composition of American Distilled Tall Oils

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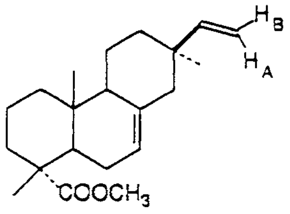
The composition of the acidic components was determined for a cross section of distilled tall oil products produced in the United States. The composition varied widely as a result of different process designs and operations. Filtration of those products that crystallize offers a potential for upgrading some distilled tall oils. In the course of this work, a new resin acid, 7,15-pimaradien-18-oic acid, was isolated and identified.

KEY WORDS: Distilled tall oil, resin acids, rosin, secodehydroabietate, tall oil.

Tall oil is the most important domestic source of rosin and a major contributor to the production of fatty acids in the United States. Nearly all U.S. tall oil is distilled. The primary products are tall oil rosin (TOR) and tall oil fatty acids (TOFA); TOR and TOFA products are defined as containing a minimum of 90% resin acids or 90% fatty acids, respectively. Other distillation cuts of mixed rosin and fatty acids not meeting this 90% minimum are grouped together as distilled tall oils. The yields and characteristics of TOR and TOFA depend on the design and operation of the distillation process, as does the byproduct distilled tall oil. The object of this study was to characterize American distilled tall oils and to identify their principal components.



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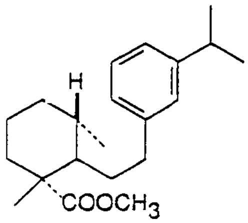

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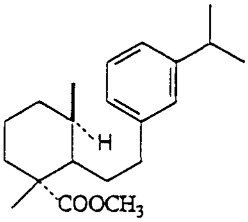

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EXPERIMENTAL PROCEDURES

Distilled tall oil samples were obtained from several tall oil fractionators. The DEAE-Sephadex method (1) was used to determine the contents of neutral and of acidic (fatty and resin acids) materials and to provide the acidic fraction for gas-liquid chromatography (GLC) analysis. GLC analysis of the methylated (CH_2N_2) acidic fractions was done with a 23-m BDS fused silica column (2,3) at a column temperature of 185°C with authentic samples for component identification; to resolve the composition of overlapping peaks, supplementing data were obtained with a 15-m DB-1 (methyl silicone) fused silica column operated at an oven temperature of 170°C.

Isolation of methyl 7,15-pimaradien-18-oate [*Compound I*]. Distilled tall oil sample F (25 g) was methylated with CH_2N_2 in Et_2O-MeOH (9:1). After removing the Et_2O-MeOH solvent by flash evaporation, 950 mL of MeOH-H_2O (2:1) and 31 g KOH pellets were added to the methylated mixture. The caustic solution was heated rigorously on a steam bath with frequent stirring for 90 min under a stream of N_2. The partially saponified mixture was acidified with 144 mL of 10% (v/v) conc. H_2SO_4 and extracted three times with petroleum ether. After the combined petroleum ether layers were washed and dried, the mixture was chromatographed on 250 g neutral alumina (4), and 9 g neutrals were eluted with 300 mL Et_2O (75% yield). The neutral fraction was subjected to repetitive argentative resin chromatography (5) before yielding methyl 7,15-pimaradienoate (98% by GLC). $[\alpha]^{25}_{D} = -28.8°$ ($CHCl_3$; *c* 1.3); ^{1}H nuclear magnetic resonance (NMR) ($CDCl_3$): δ 0.83 (Me-20), 0.96 (Me-17), 1.25 (Me-19), 2.25 (*dd*, J = 1.7, 14.6 Hz, 1H, H-14), 3.64 (OMe), 4.96 (*dd*, J = 1.8, 18.2 Hz, H-16B), 4.97 (*dd*, J = 1.8, 10.7 Hz, H-16A), 5.30 (*br m*, $w_{1/2}$ = 11 Hz, H-7), 5.67 (*dd*, J = 10.7, 18.2 Hz, H-15); the ABX exocyclic vinyl system of H-15 and -16 is described in detail elsewhere (6). ^{13}C NMR ($CDCl_3$): δ 15.2 (C-20), 17.4 (C-19), 18.1 (*t*, unassigned), 30.2 (C-17), 35.2 (C-10), 37.2 (*t*, unassigned; C-13 may overlap this resonance), 38.2 (C-12), 38.9 (C-1), 45.4 (C-5), 46.0 (C-14), 46.7 (C-4), 51.8 (OMe), 52.3 (C-9), 112.9 (C-16), 120.2 (C-7), 136.1 (C-8), 145.9 (C-15), 179.1 (C-18); ^{13}C NMR assignments were made on the basis of short-range (XHCORR) and long-range (XHCORR, COLOC) 2D correlations and with the DEPT program to determine carbon substitution. Infrared (IR) (film, cm^{-1}): 3089 (w), 1638 (w), and 830 (w) (ring vinyl system at C-7 and C-8); 3089 (w), 1638 (w), 1383 (m), 1005 (m), and 910 (s) (exocyclic vinyl at C-15 and C-16); 1727 (s) (COOMe), 2943 (s), 2920 (s), 2862 (s), 2840 (s), 2819 (m), 1458 (s), 1442 (s), 1432 (s), 1185 (s), 1147 (s), 1130 (s), 1110 (m), 683 (w), 658 (w). Mass spectra (MS) [*m/z*(%)]: 316 (60), 301 (43), 274 (20), 256 (100), 241 (95), 227 (8), 214 (10), 201 (10), 187 (17), 173 (15), 159 (14), 148 (39), 133 (42), 121 (60), 105 (60), 91 (50), 79 (50), 67 (35), 55 (55). A few milligrams of the methyl 7,15-pimaradien-18-oate were converted by acid isomerization in anhydrous HCl in $CHCl_3$ at 0°C for 5 hr (7) to the 8,15-pimaradienoate, identified by GLC retention characteristics and the NMR spectrum (8).

Secodehydroabietates. Chromatography of the whole distilled tall oil on silica gave a fraction with 1:1 petroleum ether-ethyl ether, preceding most of the resin and fatty acids, that was enriched in the secodehydroabietic acids.

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Following removal of the methyl pimarates and isopimarates by argentative resin chromatography (5) of this (methylated by CH_2N_2) fraction, a mixture of two methyl secodehydroabietates was obtained. Subsequent chromatography on silica with 0–0.5% diethyl ether in petroleum ether gave Compounds II and III in sufficient purity for identification by GLC retention characteristics and by NMR. High-performance liquid chromatography (HPLC) on 250- × 10-mm Cyclobond I (β-cyclodextrin-silica, Advanced Separation Technologies Inc., Whippany, NJ) with 0.15% THF-hexane provided pure II. The HPLC fraction further enriched in III also contained a component that, based on GPC, HPLC, and GLC retention characteristics, probably was also a secodehydroabietate.

RESULTS AND DISCUSSION

The general characteristics of U.S. distilled tall oils are summarized in Table 1. The content of neutrals and acids was determined by the DEAE-Sephadex method (1). Because of the low neutrals content in most samples, the nonsaponifiable contents were not determined. With the exception of sample D, quantitative or near-quantitative recovery was obtained for all samples; sample D may have contained dimers [conditions for quantitative elution have not been determined (1)] or more acidic materials. Most samples had a higher content of fatty acids than of resin acids, except for the viscous sample G and the partially crystalline samples H and I. The liquid portion of samples H and I was similar to that of the other distilled tall oils, but the crystalline portion of sample I approached the resin acid content necessary to be classified as a tall oil rosin. Washing of the crystals with a suitable cold organic solvent could well result in a different type of tall oil rosin.

Preliminary analysis of U.S. distilled tall oil products showed that the common tricyclic abietic- and pimaric-type resin acids and the usual 18- and 20-carbon fatty acids accounted for the majority of the components in the acid fractions. One unidentified minor component, a resin acid [as indicated by the retention behavior on GPC (9)], comprised as much as 2.4% of distilled tall oil and had GLC retention characteristics (as the methyl ester) that did not match any of an extensive listing of pine-derived resin acid methyl esters (2). The component was isolated and identified as follows.

The first step was to remove most of the fatty acids. A distilled tall oil intermediate sample containing 2–3% of the unknown resin acid was methylated with ethereal diazomethane and the primary (fatty) esters preferentially saponified with aq. KOH. The partially saponified mixture was acidified and extracted into petroleum ether. The fatty acids were then removed from the resin esters by adsorption onto neutral alumina (4), yielding a resin ester mixture with *ca.* 5% of the unknown resin ester. This mixture was subjected to repetitive argentative resin chromatography (5) before it yielded the highly enriched unknown resin acid ester (98% by GLC). The elution volume of the unknown resin acid ester for the silver column was between methyl sandaracopimarate and methyl isopimarate, giving a misleading indication at the time that it was an isopimarate isomer.

^1H NMR of the isolate showed three methyl signals (δ 0.83, 0.96, and 1.25), an ABX exocyclic vinyl system, and a single vinyl ring proton (δ 5.30 *br m*, $w_{1/2}$ = 11 Hz) characteristic of a methyl pimaradienoate or its C-13 epimer. The three possible locations for the trisubstituted ring double-bond system were between carbons 5 and 6, 7 and 8, or 9 and 11. Also present was an isolated resonance for a single allylic proton at δ 2.25 (*dd*, J = 1.7, 14.6 Hz), which, as indicated by homonuclear decoupling, was not coupled to the lone vinyl ring proton at δ 5.30. The absence of coupling eliminated the 5(6) and 9(11) structures because both have allylic methylene protons that would be coupled to the vinyl ring proton, leaving 7,8 as the only possible location for the double bond. Short-range heteronuclear 2D NMR further correlated the allylic proton at δ 2.25 with a methylene carbon at 46.0, which, in turn, was correlated to H-17 methyl (δ 0.96) by long-range 2D NMR. The allylic proton at δ 2.25 was also correlated to both the quaternary (δ 136.1) and tertiary (δ 120.2) carbons of the ring vinyl system (*i.e.*, not part of the ABX exocyclic vinyl system). The allylic proton 2D

TABLE 1

Gross Compositional Characteristics of American Distilled Tall Oils[a]

Tall oil sample	Composition (%)				
	DEAE-Sephadex separation			Acids	
	Neutrals	Acids	Recovery	Fatty acids	Resin acids
A	2.7	97.5	100.2	63	37
B	3.0	97.0	100.0	60	40
C	2.3	96.2	98.5	65	35
D	5.2	86.9	92.1	60	40
E	3.6	96.4	100.0	68	32
F	3.9	96.1	100.0	53	47
G	5.2	94.8	100.0	23	77
H	6.6	93.4	100.0	47	53
H_L	7.9	92.1	100.0	55	45
H_{Xs}	4.1	95.9	100.0	29	67
I	4.0	96.0	100.0	45	55
I_L	4.7	95.3	100.0	62	38
I_{Xs}	1.9	98.1	100.0	17	83

[a] For partially crystalline DTO samples H and I, subscripts L and Xs designate liquid and crystalline portions, respectively; sample H consisted of 72% liquid and 28% crystalline portions, and I consisted of 67% liquid and 33% crystalline portions.

TABLE 2

Composition of Fatty and Resin Acids in American Distilled Tall Oils[a]

	Acid composition of various tall oil samples[b]												
Acid type	A	B	C	D	E	F	G	H	H_L	H_{Xs}	I	I_l	I_{Xs}
Fatty acid													
16:0 (palmitic)	0.4	0.4	0.8	1.1	0.8	0.3	0.2	0.1	<0.1	0.1	0.8	0.9	0.3
18:0 (stearic)	1.4	1.2	1.0	1.0	1.1	0.7	0.3	0.5	0.4	0.5	0.9	1.1	0.4
18:1 (oleic)	26.2	21.6	16.0	17.1	16.8	6.9	2.9	4.6	5.2	2.4	14.0	18.7	4.5
18:2 (linoleic)	19.1	15.3	11.5	13.2	12.9	4.8	1.9	3.4	3.9	1.9	11.2	15.0	3.6
Unidentified	1.7	1.1	1.1	1.5	1.1	1.1	0.1	0.5	0.6	0.4	0.7	1.0	0.2
18:2 (9,11 *ct*)	0.9	1.5	0.9	0.9	0.8	1.2	—	0.2	0.3	0.4	0.4	1.6	0.4
18:2 (9,11 *tt*)	2.0	5.6	6.6	4.0	8.4	8.7	—	4.3	5.4	2.7	3.4	4.6	1.0
18:3 (5,9,12)	1.4	0.8	0.7	1.0	0.3	0.2	0.1	0.2	0.2	0.1	0.8	1.1	0.3
20:0	0.6	1.6	1.3	1.6	1.3	1.6	1.1	2.9	1.7	6.1	0.8	0.6	0.2
20:1	0.6	1.0	2.3	2.4	2.2	2.7	1.4	4.1	5.0	2.1	0.9	1.4	0.3
20:2	0.8	1.4	3.5	2.4	3.4	4.2	2.2	5.1	6.3	2.5	1.4	2.1	0.4
20:3	3.3	5.7	13.4	7.7	14.6	14.9	5.7	17.2	21.0	9.6	6.2	8.3	1.9
Resin acid													
Secodehydroabietic (II)	0.7	0.8	2.0	2.8	1.8	3.0	0.7	1.7	1.9	0.6	0.6	0.9	0.3
Secodehydroabietic (III)	0.6	1.0	2.0	1.9	2.2	2.0	1.0	1.5	1.7	0.7	0.7	0.9	0.2
8,15-isopimaradienoic	2.4	5.6	9.6	11.6	7.4	12.3	11.1	11.4	12.3	8.1	2.4	2.3	2.5
8,15-pimaradienoic	1.3	2.4	8.5	2.4	3.0	12.5	5.3	10.6	8.8	12.6	1.2	0.9	1.6
Pimaric	4.2	5.4	2.6	7.1	7.2	4.8	11.4	10.4	3.9	27.3	5.9	5.8	6.7
Sandaracopimaric	1.5	2.2	1.6	1.9	1.7	2.2	4.6	3.9	2.0	7.2	2.0	1.8	2.5
7,15-pimaradienoic (I)	0.2	0.4	1.6	1.0	0.3	2.4	0.9	2.1	2.2	2.4	0.2	0.2	0.3
Palustric	2.1	2.0	0.5	0.8	1.1	0.3	4.2	0.8	0.8	0.9	4.6	3.4	6.2
Isopimaric	4.2	5.3	1.9	2.1	4.1	2.8	11.1	3.5	3.5	3.4	6.4	4.1	10.3
Abietic	13.3	8.4	2.2	2.9	1.9	2.4	15.4	3.0	3.7	2.9	20.4	11.5	33.4
Dehydroabietic	6.3	5.5	1.8	4.6	1.2	1.9	9.5	3.0	3.2	2.3	8.2	3.8	16.4
Neoabietic	0.8	0.6	0.1	0.3	0.1	0.1	1.4	0.2	0.1	0.5	2.0	2.0	1.4
(Total resin acids)	37	40	35	40	32	47	77	53	45	71	55	38	83

[a] Data based on GLC with a 23-m BDS fused silica column (185°C); supplemental information obtained for 20:0 and pimarate/8,15-pimaradienoate with a 15-m DB-1 thin-film column at 170°C.

[b] Percentage of total acids.

NMR correlations place this methylene unambiguously between C-13 and the ring vinyl system. The orientation of the exocyclic vinyl was determined by acid-catalyzed isomerization of the unknown resin acid to 8,15-pimaradienoate (short-range 2D NMR correlated H-17 with δ 30.2 in the ^{13}C dimension). There is still ambiguity about the stereochemistry at C-9—the mechanism for isomerization involves deprotonation and subsequent reprotonation at C-9, possibly resulting in a reversal from α to β orientation for H-9. NOE experiments were carried out to determine precisely the orientation of H-9, but these were difficult to interpret because of resonant frequency overlap of H-9 with other protons. However, NOE irradiation of H-9 (*ca.* δ 1.7 as determined by short-range 2D NMR correlation) showed no effect at Me-20 (δ 0.83) and *vice versa.* If H-9 is β, a clear NOE is expected between H-9 and (axial) Me-20. Because no effect was observed, it is likely that the α orientation of H-9 is unaffected by the isomerization reaction. Thus, we conclude that the unknown resin acid is 7,15-pimaradien-18-oic acid as found in the original distilled tall oil intermediate fraction. The C-4 epimer of enantio-I has been isolated from *Helianthus* species (10).

In a GLC examination of the oleoresins of slash and loblolly pines, the two major species used in the production of tall oil, no methyl 7,15-pimaradienoate was observed. Methyl communate is a major component of slash pine oleoresin and the closest in relative retention to methyl 7,15-pimaradienoate. However, GLC analyses on both DB-1 at 190°C (separation factor, $\alpha = 1.04$) and BDS at 185°C ($\alpha = 1.024$) gave adequate resolution between the two components, avoiding any possible confusion about the presence or absence of methyl 7,15-pimaradienoate. Therefore, 7,15-pimaradienoic acid appears to be an isomerization artifact of distillation. The 8,15-pimaradienoic and isopimaradienoic acid isomers are artifacts of the same process and are found in higher proportions because tetra-substituted ring olefins are more stable than tri-substituted ring olefins. The degree of isomerization of pimaric, sandaracopimaric, and isopimaric acids to the 8,15- and 7,15-pimara- and isopimaradienoic acids varies between samples (Table 2) as a result of differences in processing techniques.

The two secodehydroabietic acids, each usually present at about 1–2% of the distilled tall oil acids, were isolated as the methyl esters. Herz and Mohanraj (11) showed by an unambiguous synthetic sequence that the C-5 stereochemistry (C-5 of the parent levopimaric acid is C-2 in the rigorous cyclohexanecarboxylate nomenclature of the secodehydroabietate products) is not changed in the products from the reaction of levopimaric acid with base (12) or the secodehydroabietate isolated from distilled tall oil (13). Methyl secodehydroabietates [II] and [III] thus differ only by the stereochemistry at C-2 (cyclohexanecarboxylate). GLC and NMR data for these two compounds are given in Table 3.

The composition of the fatty and resin acids in the distilled tall oils is given in Table 2. In general, the table

TABLE 3

GLC Retention and NMR Characteristics of the Methyl Secodehydroabietates[a]

Compound	GLC ($r_{pimarate}$)		NMR (methyl resonances)
	BDS	DB-1	
2β-[2′-m-isopropylphenyl)ethyl]-1β,3α-dimethylcyclohexane-carboxylate [II]	0.810	0.798	1.252 *s* J = 6.9, 1.155 *s*, 0.910 *d* *J* = 6.8
2β-[2′-m-isopropylphenyl)ethyl]-1β,3β-dimethylcyclohexane carboxylate [III]	0.904	0.862	1.237 *s* J = 6.8, 1.138 *s*, 1.017 *d* *J* = 6.3

[a] GLC data per conditions of Table 2. An impurity in III (a secodehydroabietate?) had GLC retention of 0.853 (BDS) and 0.829 (DB-1).

TABLE 4

Composition of Pimaric- and Isopimaric-Type Acids Comprising Resin Acids of American Distilled Tall Oils[a]

Acid type	Acid composition of various tall oil samples (%)[b]								
	A	B	C	D	E	F	G	H	I
8,15-Isopimaradienoic	6.5	1.4	27.5	29.0	23.1	26.2	14.4	21.6	4.4
8,15-Pimaradienoic	3.5	6.0	24.3	6.0	9.3	26.6	6.9	20.0	2.2
Pimaric	11.3	13.5	7.4	17.8	22.5	10.2	14.8	19.7	10.7
Sandaracopimaric	4.1	5.5	4.1	2.5	5.3	4.7	6.0	7.4	3.6
7,15-Pimaradienoic	0.6	1.0	4.6	2.5	0.9	5.1	1.2	4.0	0.4
Isopimaric	11.3	13.3	5.4	5.3	12.8	6.0	14.4	6.6	11.2
(Total pim/isopim acids)	38	62	74	65	74	79	58	79	33

[a] Data recalculated from Table 2.

[b] Percentage of total resin acids.

does not include components comprising less than 1% of total content. The components and composition of the fatty acid fraction are as expected; they include, for example, the effects of the base-catalyzed isomerization of linoleic acid that occurs during pulping. The resin acid components and composition in the distilled tall oils are skewed toward the lowest boiling of the resin acids [*cf.* GLC retention of the methyl esters on nonpolar liquid phases such as the methyl silicones (3)]. As a group, the pimaric- (pimaric acid and the 7,15 and 8,15 isomers) and isopimaric-type acids (isopimaric and sandaracopimaric acids and the 8,15 isomer) predominate, particularly for samples B to H (Table 4). The highest degree of isomerization (*i.e.*, the largest relative amounts of 8,15 isomers) among these acids occurred in samples C to F and H (as high as 80%); the content of compound I parallels the overall isomerization in these samples with the exception of E. In E, the overall isomerization to the 8,15 derivative is considerably greater for the isopimaric acids than for the pimaric acids.

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