Capillary Gas Chromatography-Mass Spectrometry of Resin Acids in Tall Oil Rosin

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ABSTRACT

The resin acid composition of Finnish tall oil rosin was investigated by gas chromatography and mass spectrometry employing open tubular capillary columns. On a column coated with 1,4-butanediol succinate, 16 resin acids found in tall oil rosin samples were well resolved, and mass spectra could be recorded. All resin acids were confirmed to be of the pimaric and abietic types by gas chromatography-mass spectrometry. Eight of the acids were not detected in the corresponding crude tall oils and evidently had been formed during the technical distillation process. The presence of 8,15-pimaradien-18-oic and 8,15-isopimaradien-18-oic acids in the rosin, but not in the crude tall oil, indicates that the pimaric type acids also undergo extensive isomerization during tall oil distillation. Additionally, three dihydroabietic acids and two acids with identical mass spectra, tentatively stereoisomers of 7,9(11)-abietadien-18-oic acid, were formed during the distillation process.

INTRODUCTION

The composition of the resin acids in Finnish crude tall oil recently was reported (1). The resin acid composition of the tall oil rosin differs significantly from that of crude tall oil owing to decomposition and isomerization reactions taking place during the distillation process. The resin acid composition of rosins from American and other sources has been investigated by Lawrence (2) and Joye (3). However, adequate data have not been reported for Scandinavian tall oil rosin. The object of this study was to investigate the resin acid composition of Finnish distilled tall oil rosins and to determine the change in component composition effected by the distillation conditions.

Gas chromatography (GC) and mass spectrometry (MS) have been commonly applied to resin acid analysis (4-10). Also open tubular capillary columns have been tested on resin acids (11,12), but no detailed study has been made on the suitability of capillary columns in GC-MS analysis of complex resin acid mixtures.

EXPERIMENTAL PROCEDURES

Samples Investigated

Samples of crude tall oil and tall oil rosin were obtained from two Finnish distillation plants, each using a continuous distillation system with 4-6 distillation columns. The rosin fraction was taken from the bottom of the second column.

The rosin samples investigated had acid numbers, 154.5-157.7 (13); saponification numbers, 163.9-174.4 (14); and resin acid contents, 79.2-81.4% (15). Corresponding samples of crude tall oil gave acid numbers, 148.6-150.0 (plant A) and 134.2 (plant B); saponification numbers, 156.0-157.0 (A) and 162.8 (B); and resin acid contents 38.2-39.9%. The crude tall oils of plant A were derived from pine (*Pinus silvestris*) alone, whereas the crude oil of plant B contained birch (*Betula verrucosa* and *B. pubescens*) constituents as well.

Sample Preparation

The free acids were isolated by extraction with aqueous KOH solution, as reported earlier (1). The rosin samples contained 84.4-88.5% free acids and the crude tall oils 84.8-86.1% (A) and 79.5% (B). The acids were methylated with diazomethane and the methyl esters analyzed by GC and GC-MS.

GC

All GC analyses were performed with a Varian model 2100 gas chromatography equipped with flame ionization detectors. Nitrogen was used as carrier gas. An electronic integrator, Varian model 477, was used for peak area measurement. The composition of the resin acids was calculated directly from the peak areas.

Stainless steel open tubular columns were prepared in our laboratory by coating with Apiezon L (Varian Aerograph) or 1,4-butanediol succinate (BDS), HI-EFF-4BP (Applied Science Laboratories, State College, Pa.) using the dynamic coating method (16). The columns had a length of 45 m and inside diameter of 0.50 mm. Glass capillary columns of 40-45 m in length with an inside diameter of 0.35-0.40 mm were coated with methyl silicone OV-101 (Applied Science Laboratories), applying the static coating method.

A glass column coated with the liquid phase SP-1000, a substituted polyethylenglycol terephtalate, also was tested. The column had a length of 25 m and an inside diameter of 0.25 mm.

When capillary columns were employed, the GC was equipped with an injection splitter of our construction. Sample volumnes of 0.1-0.2 μliter were injected and split in the ratio 1:50.

GC-MS

The same capillary columns were used in a LKB 9000 GC-MS, after providing it with an injection splitter and a make-up gas device. Mass spectra were recorded at 70 eV ionization potential. The temperature of the molecule separator was 250 C and the temperature of the ion source 290 C. The ion accelerating voltage was kept at 3.5 kV. At least two mass spectra were scanned from each peak. The scanning time was 2 sec.

RESULTS AND DISCUSSION

Separation and Identification of Resin Acid Methyl Esters

Far better separation was achieved with all the capillary columns than with any packed column. The BDS column was found to be the most selective; all the 16 resin acids listed in Table I could be separated as their methyl esters (Fig. 1). Peak overlapping could not be avoided on the nonpolar Apiezon L and OV-101 columns despite the higher number of theoretical plates (Fig. 2). The SP-1000 glass column gave a similar separation to the BDS column but did not resolve the component 10.

Relative retention times for the resin acid methyl esters are given in Table I. The relative retention times were found to change appreciably with column aging, this being especially true for the polar BDS and SP-1000 columns which gave lower values after some weeks use. The observed retention times show good agreement with values reported

TABLE I

Probable Identity and Relative Retention Times of Tall Oil Resin Acid Methyl Esters

GC peak number	Resin acid methyl ester				Relative retention time[a]				
	Systematic name[b]	Common name	Abbreviation		1,4-Butanediol succinate		Apiezon L 235 C	SP-1000 190 C	OV-101 200 C
					205 C[c]	205 C[d]			
1	8,15-Isopimaradien-18-oate		8,15-IP[e]		0.875	0.880	0.875	0.885	0.875
2	8,15-Pimaradien-18-18-oate		8,15-P[e]		0.980	0.975	0.955	0.975	0.945
3	8(14),15-Pimaradien-18-oate	Pimarate	P		1.000	1.000	1.000	1.000	1.000
4	x-Abieten-18-oate	Dihydroabietate	DiAb$_1$[e]		1.110	1.085	1.260	1.135	
5	8(14),15-Isopimaradien-18-oate	Sandaracopimarate	Sa		1.120	1.110	1.070	1.095	1.050
6	13-Abieten-18-oate	Dihydroabietate	DiAb$_2$[e]		1.175	1.130		1.175	
7	x-Abieten-18-oate	Dihydroabietate	DiAb$_3$[e]		1.205	1.160	1.330	1.225	
8	x,x-Abietadien-18-oate		x,x-Ab[e]		1.280	1.245	1.135	1.315	1.085
9	8,13-Abietadien-18-oate	Palustrate	Pal		1.370	1.315	1.225	1.420	1.220
10	7,9(11)-Abietadien-18-oate		7,9(11)-Ab[e]		1.405	1.340	1.350		
11	7,15-Isopimaradien-18-oate	Isopimarate	IP		1.465	1.420	1.270	1.450	1.180
12	13β-Abieta-7,9(11)-dien-18-oate		13β-7,9(11)Ab[e]		1.640	1.545	1.455	1.690	1.370
13	7,13-Abietadien-18-oate	Abietate	Ab		2.175	2.030	1.695	2.110	1.550
14	8,11,13-Abietatrien-18-oate	Dehydroabietate	DeAb		2.280	2.080	1.380	2.145	1.320
15	8(14),13(15)-Abietadien-18-oate	Neoabietate	Neo		2.480	2.275	1.950	2.430	1.810
16	6,8,11,13-Abietatetraen-18-oate	Dehydrodehydroabietate	DeDeAb		2.650	2.385	1.920	2.470	1.755

[a]Relative to methyl pimarate.
[b]In accordance with recent proposals (17).
[c]With newly prepared column.
[d]With column used for one month.
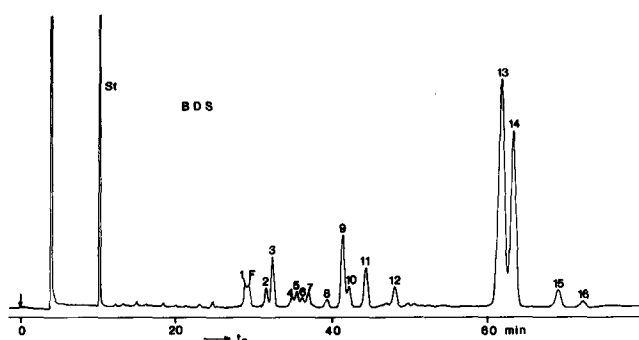[e]Acids present in tall oil rosin but not in crude tall oil.

FIG. 1. Gas chromatographic analysis of tall oil rosin as methyl esters. Column: 45 m x 0.50 mm inside diameter open tubular stainless steel coated with 1,4-butanediol succinate (BDS). Carrier gas (He) flow rate: 2.3 ml/min. Column temperature 205 C. Instrument: LKB 9000 gas chromatograph-mass spectrometer. For identities of resin acid methyl ester peaks see Table I. St denotes methyl heptadecanoate added as internal standard and (F) methyl docosanoate (22:0 n).
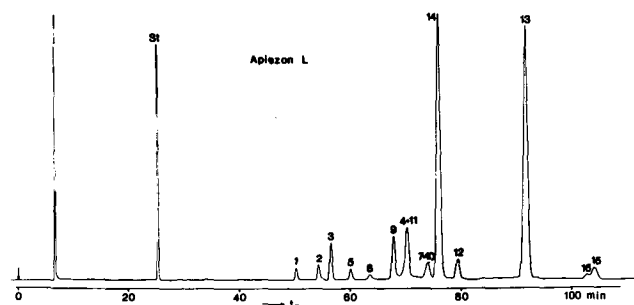

FIG. 2. Gas chromatographic analysis of tall oil rosin as methyl esters. Column: 45 m x 0.50 mm inside diameter open tubular stainless steel coated with Apiezon L. Carrier gas (N$_2$) flow rate: 1.7 ml/min. Column temperature 235 C. Instrument: Varian model 2100. Peak numbering as in Figure 1 and Table I.

TABLE II

Relative Abundances for Typical Ions in Recorded Mass Spectra

GC peak number	Resin acid methyl ester	Base peak m/e	Parent ion M, m/e	M	M-15, -CH$_3$	M-43, -C$_3$H$_7$	M-59, -COOCH$_3$	M-60, HCOOCH$_3$	M-75, -CH$_3$-HCOOCH$_3$	M-103, -C$_3$H$_7$-HCOOCH$_3$	Other characteristic ions, m/e/%
	Abbreviation										
1	8,15-IP	241	316	42	51	2	53	14	100	7	173/28, 274/12
2	8,15-P	241	316	43	56	0	33	16	100	5	173/22,, 274/10
3	P	121	316	8	6	0	10	3	5	0	180/19, 181/14
4	DiAb$_1$	121	318	18	26	33	24	13	62	52	181/21, 187/19
5	Sa	121	316	9	9	0	10	3	5	0	180/12, 181/14
6	DiAb$_2$	121	318	5	1	20	10	3	2	42	136/23, 181/21
7	DiAb$_3$	121	316	16	26	28	24	12	71	40	181/17, 187/23
8	x,x-Ab	241	316	48	52	20	48	78	100	17	121/75, 148/70
9	Pal	301	316	78	100	3	10	7	93	22	105/92, 149/63
10	7,9(11)-Ab	241	316	89	11	30	33	51	100	43	187/46, 201/52
11	IP	241	316	37	20	0	58	52	100	11	187/45, 287/19
12	13β-7,9(11)-Ab	241	316	83	13	41	41	52	100	56	187/57, 201/68
13	Ab	256	316	88	12	20	38	100	67	54	121/95, 136/55
14	DeAb	239	314	11	13	0	3	0	100	3	
15	Neo	135	316	17	0	0	3	1	1	0	121/35, 148/23
16	DeDeAb	237	312	55	10	0	9	10	100	26	195/42, 197/63

earlier for packed columns with polar and nonpolar phases (1,7).

The improved separation obtained with the capillary columns enabled the recording of mass spectra of all resin acid methyl esters. Table II lists the relative abundances for typical fragment ions.

The main acid components could be identified by comparing retention times and mass spectra with those of the authentic reference samples previously studied in our laboratory (1). Reference compounds were not available for all the minor resin acids detected in tall oil rosin. The assignments of these minor acids could be based upon GC-MS data only and are thus tentative.

The components 1 and 2 gave mass spectra similar to those reported by Zinkel, et al., (8) for methyl 8,15-isopimaradien-18-oate and methyl 8,15-pimaradien-18-oate and, like these, eluted before pimaric acid on all columns. The mass spectra of these two stereoisomers were practically identical. A reference sample of 8,15-isopimaradien-18-oate gave identical GC-MS values with 1.

8,15-Isopimaradienic acid has been shown to be a natural constituent of some pines (3,18) but has not been found in Scots pine (*Pinus silvestris*). 8,15-Pimaradienic acid has been isolated from a tall oil intermediate distillate fraction, besides 8,15-isopimaradienic and a secodehydroabietic acid (19). We also detected small amounts of a similar secodehydroabietic acid in Finnish distilled tall oil. However, this acid was not found in tall oil rosin.

Three methyl esters with mol wt of 318 were separated on the BDS column. Of these, the components 4 and 7 gave almost identical mass spectra and, thus, seem to be stereoisomers. The mass spectra showed the parent ion at m/e 318 and the base peak at 121. Other abundant peaks were at m/e 215, 243, 259, 275, and 303, indicating abietenic structure; but 4 and 7 could not be identified as any of the characterized dihydroabietic acids (20). The peaks 4 and 7 may possibly be mixtures of the two 8-abietenoates and the two 8(14)-abietenoates.

The acid 6 gave a mass spectrum similar to that of 13-abieten-18-oate (10). A possibly identity of 6 is also 8α-abiet-13-en-18-oate (21). GC-MS data have not, however, been reported for this acid.

Peak 8 was well resolved on all capillary columns and gave identical mass spectra with different columns. The parent ion was at m/e 316. Abundant MS peaks at m/e 241, 256, 301, 257, 273, and 213 indicate abietadienic structure. Possible structure choices may be 8,11- and 9(11),12-abietadien-18-oates described by Herz and White (22), after the preparation of the original manuscript for this article.

Peak 12 gave GC-MS characteristics in accordance with methyl 13β-abieta-7,9(11)-dien-18-oate (8). Peak 10 gave a practically identical mass spectrum with the base peak at m/e 241 and with other principal peaks at m/e 316, 131, 201, 256, 187, 213, and 257. It appears that the components 10 and 12 are stereoisomers, with component 10 possibly being the 13-α isomers of 7,9(11)-abietadien-18-oate. We believe that this isomer has not been shown previously to occur in any resin acid mixture.

The last eluted component 16 showed a mol wt of 312, and its MS resembled that reported for 6,8,11,13-abietatetraen-18-oate (10).

Changes in Resin Acid Composition Occurring During Tall Oil Distillation

The difference in resin acid composition between crude tall oils and tall oil rosins is shown in Table III. The results are remarkably similar for the two distillation plants. The clear difference between the crude oils and the rosins must be explained as a result mainly of decomposition and isomerization reactions occurring at the high temperatures, up to 280 C, maintained in the distillation process. There is

TABLE III

Resin Acid Composition (wt %) of Corresponding Crude Tall Oils and Distilled Tall Oil Rosins

Resin acid		Crude tall oils		Tall oil rosins	
Abbreviation	GC peak number	A	B	A	B
Pimaric					
P	3	11.2	11.0	4.2	3.7
8,15-P	2	—	—	2.0	2.4
Isopimaric					
IP	11	7.6	7.2	4.4	5.5
Sa	5	2.0	2.0	1.4	1.2
8,15-IP	1	—	—	1.0	1.8
Abietenic					
DiAb$_1$	4	—	—	0.8	0.5
DiAb$_2$	6	—	—	1.3	0.8
DiAb$_3$	7	—	—	1.8	1.4
Abietadienic					
Ab	13	54.6	52.9	39.9	32.5
Pal	9	2.0	4.4	4.6	5.2
Neo	15	4.8	4.3	2.4	0.8
7,9(11)-Ab	10	—	—	1.6	2.0
13β-7,9(11)-Ab	12	—	—	2.6	3.0
X,X-AG	8	—	—	1.0	0.3
Abietatrienic					
DeAb	14	17.8	18.2	30.2	37.6
Abietatetraenic					
DeDeAb	16	Trace	Trace	0.8	1.3

also a different distillative distribution of single resin acids on account of their different boiling points.

The most obvious change is the large increase in dehydroabietic acid and a corresponding decrease in abietic acid. This change may be partially explained by dehydrogenation of abietadienic acids at the high tempeatures employed. Further, disproportionation of abietadienic acids and also decomposition of oxy acids may cause the increase in dehydroabietic acid (2).

The minor resin acids (8 acids) present in rosin were not found in crude tall oil and clearly have been formed in the distillation process. None of these acids previously has been found in Finnish tall oil rosin. The formation of new isomers of both pimaric and isopimaric acids is noteworthy; these acids earlier have been reported to remain unchanged by processing at the temperatures normally encountered in tall oil distillation (2). These isomers, 8,15-pimaradien-18-oic and 8,15-isopimaradien-18-oic acids, are also of technical importance, because they have low boiling points and so concentrate as impurities in tall oil fatty acid fractions (19).

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