Improved Procedure for the Analysis (GLC) of Resin Acids

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ABSTRACT

The analysis of resin acid content of rosin and oleoresin often is affected by neutral material. This problem can be overcome by analyzing the sample before esterification.

INTRODUCTION

The major components in pine oleoresin and rosin are diterpene acids. The methyl esters of these acids have been analyzed on a number of gas liquid chromatographic (GLC) column systems (1-4). In all cases, the neutral components of the sample have been included in the analyses; and no attempt to remove these components has been reported. Recent work in our laboratory (5) has shown that commercial rosins contain 5-15% neutral components. The largest portion of these neutral components is diterpene aldehydes and alcohols and is eluted from the gas chromatograph in the same region as the resin acid methyl esters. Some of these neutral components appear as small peaks before, after, and between the peaks of the resin acid methyl esters. Others are under the methyl ester peaks and are included in the calculated percent of these components. These neutral components can be determined and corrected for by chromatographing the sample before esterification. The resin acids are not eluted from the column, and the neutrals, having retention times in the same region as the resin acid methyl esters, can be determined and the necessary corrections made.

The present work was carried out to improve the analysis of the resin acids and to obtain better agreement between the amount of acidic material from the GLC analysis and the acid number of the sample.

EXPERIMENTAL PROCEDURES

Apparatus: A Hewlett-Packard model 700 gas chromatograph with a flame ionization detector was used to analyze the resin acid methyl esters and neutral components in pine oleoresin and rosin. A 15 ft x 3/16 in. outside diameter copper column packed with 5% Versamid 900 on 70-80 mesh Gas Chrom Q operated at 250 C with a flow of 100 ml helium/min was used. The injection port and detector were maintained at 300 C. Retention times and peak areas were measured with a Vidar model 6300 digital integrator.

Analytical method: A sample of pine oleoresin or rosin (0.100 g) was weighed in a small vial and 0.010 g methyl

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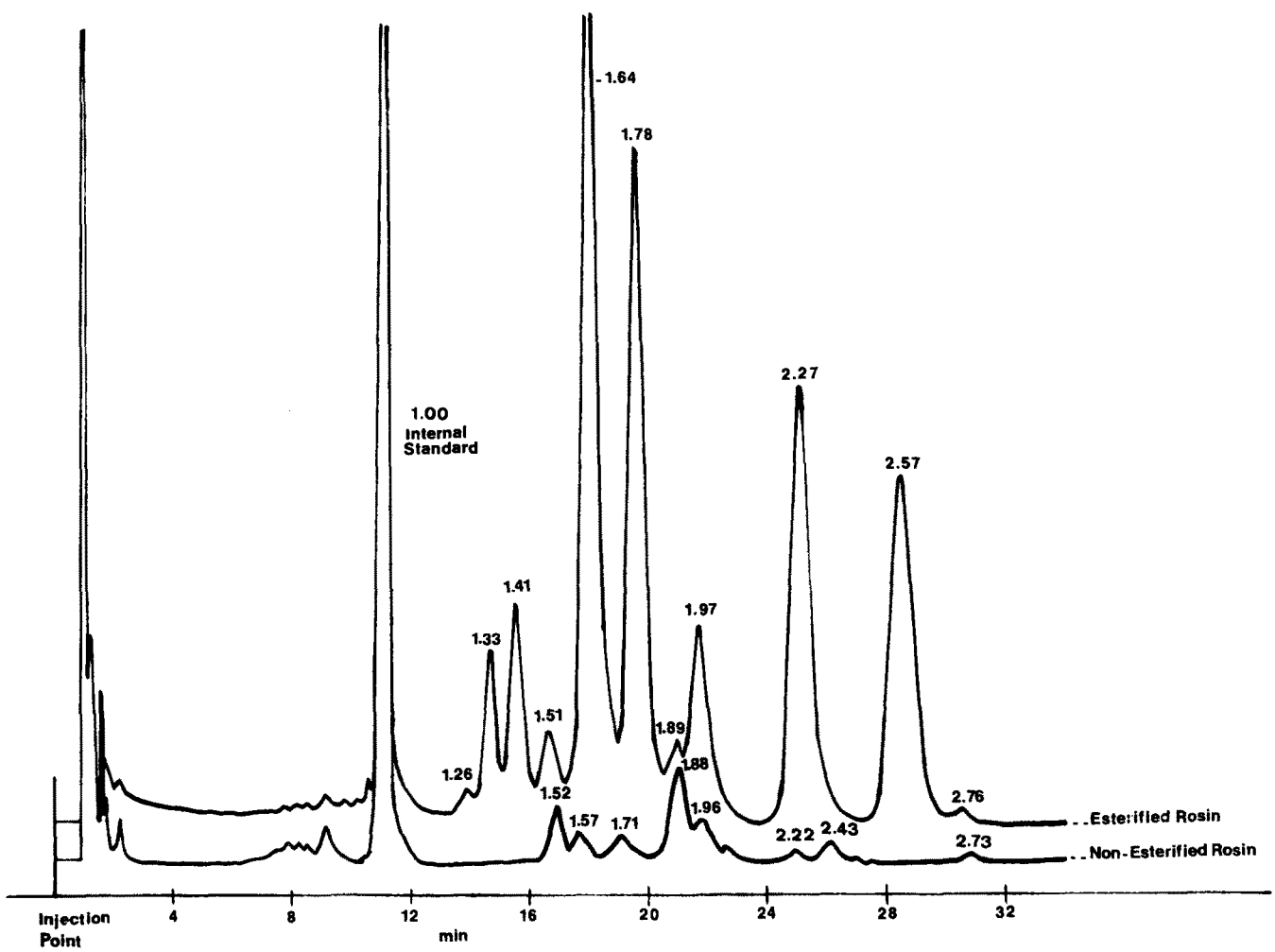

FIG. 1. Chromatogram of neutral components under acid components in gum rosin.

TABLE I

Gas Liquid Chromagraphic Analysis of Resin Acids

Sample	$\Delta^{8(9)}$-Isopimaric	Elliotinoic	Pimaric	Sandaracopimaric	Palustric and levopimaric	Isopimaric	Neutral component	Dehydroabietic	Abietic	Neutral component	Neoabietic	Neutral component	Percent off column[a]	Total acids %
	Relative retention time[b]													
	1.26	1.33	1.41	1.51	1.64	1.78	1.89	1.97	2.27	2.37	2.57	2.76		
	Percent of sample													
Pinus elliottii var. *elliottii* Rosin A.N.[c] 160														
Esterified	0.4	3.4	4.5	2.2	26.1	18.0	1.6	5.5	15.2	---	13.0	0.4	89.9	
Nonesterified	---	---	---	0.9	0.4	0.3	1.9	0.6	0.5	---	---	0.2	4.7	
Corrected acid content[d]	0.4	3.4	4.5	1.3	25.7	17.7	-0.3	4.9	14.7	---	13.0	0.2	85.2	86.5[e]
Pinus elliottii var *elliottii* Oleoresin A.N.[c] 110														
Esterified	0.7	2.9	5.1	3.2	20.5	13.5	---	6.1	6.6	---	8.1	0.6	69.0	
Nonesterified	0.2	---	---	3.0	---	0.8	---	3.7	0.5	---	0.2	0.5	10.5	
Corrected acid content[d]	0.5	2.9	5.1	0.2	20.5	12.7	---	2.4	6.1	---	7.9	0.1	58.5	59.5[e]
Pinus Lawsoni Rosin A.N.[c] 115														
Esterified	0.9	2.1	7.9	8.7	23.1	23.5	13.2	3.0	9.9	7.9	10.0	2.8	122	
Nonesterified	0.9	0.9	0.4	9.8	---	7.5	11.7	3.1	0.3	10.6	0.4	2.5	60	
Corrected acid content[d]	---	1.2	7.5	1.1	23.1	16.0	1.5	-0.1	9.6	-2.7	9.6	0.3	62	62[e]

[a]Percent of sample off column as calculated from wt of samples and internal standard and ratio of peak areas to internal standard.

[b]Relative retention time relative to methyl arachidate 1.00.

[c]Acid number of sample determined by titrating weighed sample in methanol to phenolphthalein end point with 0.1N sodium hydroxide.

[d]Corrected acid content determined by subtracting percent of nonesterified sample components from esterified sample components.

[e]Calculated percent acids in sample determined by dividing acid number by 185 (theoretical acid number of resin acid).

arachidate in 1 ml ether added. As soon as the sample dissolved, 1-2 μliters were injected into the gas chromatograph. The chromatogram obtained shows only the neutral components and the internal standard from which the percent neutrals in the sample are calculated. The sample solution then is esterified with diazomethane or titrated with tetramethylammonium hydroxide and 1-2 μliter injected into the gas chromatograph. The chromatogram from this run shows the resin acid methyl esters and the neutral components. The percent of the sample from this run includes the resin acid methyl esters and the neutral components. Sample size was 0.2 tenths-2.0 μliter in a 10% solution. No differences were observed in linearity when up to 10 μliter were injected.

The data from both chromatograms are recorded, and the relative retention times and relative wt readily are calculated and converted to percent. The percent of the esterified sample off the column, less the percent of the neutral components, equals the amount of acids in the sample. By subtracting the neutral component under each methyl ester, the actual value of each component is determined.

The acid number of each rosin sample was determined by titrating a weighed sample, dissolved in methanol, to a phenophthalein end point with 0.1N sodium hydroxide. The calculated percent acids in each sample were determined by dividing the acid number of the sample by 185 (the theoretical acid number of resin acid).

RESULTS AND CONCLUSIONS

Table I summarizes results from the analyses of the neutral and acid components in three rosin samples. The corrected percent of acid components agrees closely with the calculated percent acids determined from the acid number of the sample. The percent of each component also compares with the amount of acid that can be isolated from the rosin.

Figure 1 shows the GLC curves of the methyl esters and the neutral components in slash rosins (*Pinus elliottii* var. *elliottii*). These curves show other neutral peaks that are not included in Table I. Only those peaks that are in the same section of the curve as the methyl esters are used, since they are included in the total area of the methyl ester analyses.

Corrections for differences in response of the methyl esters and neutral components are not necessary due to the subtraction procedure.

Analyses of 20 pine oleoresins and rosins by the described procedure gave excellent results. Pine oleoresins containing more than 50% neutral components and rosins containing less than 5% neutral components were analyzed, and agreement was good between the titrated acid number and the percent acid as determined by this procedure.

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