Composition of Neutral Oils from Rosin

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ABSTRACT

The neutral fractions from gum, wood and tall oil rosins were isolated and examined by gas chromatography. The major components found were diterpene aldehydes and alcohols. Smaller quantities of diterpene hydrocarbons and monoterpenes were identified. The differences in the composition and concentrations of the neutral fractions appear to explain some of the differences in physical characteristics of the three types of rosin.

INTRODUCTION

The production of rosin in this country has averaged about one billion pounds per year for the past 60 years. This rosin is composed of a mixture of diterpene acids and neutral materials. A great deal of information is available on the composition of the acid portion of rosin, but very little is known of the composition of the neutral fraction. This fraction makes up 4-15% of commercial rosins and can have an important influence on the characteristics of the rosin and its derivatives. Enos et al. (1) stated "The composition of the neutral fractions of rosins is not well understood, and it is most probable that in this respect gum, wood and tall oil rosins differ." Erdtman and Westfelt (2) and Westfelt (3) reported on the neutral constituents from extracts of wood from *Pinus silvestris*. Harris and Sanderson (4) reported isopimarinal in commercial gum rosin. Lundquist and Kautto (5) reported the neutral carbonyl compounds in tall oil. Other reports (6-11) have indicated the presence of sesquiterpenes, aldehydes, alcohols, steroidal compounds and stilbene derivatives in various rosins. Although these references report numerous individual components isolated from rosin, no complete analysis of rosin neutrals has been published. Insofar as we can determine, this is the first attempt to analyze the whole neutral fraction from rosin.

The present work was carried out to determine the difference in the neutral fraction from gum, wood and tall oil rosins. Each rosin was separated into neutral and acid portions and the neutral portion analyzed by gas chromatography.

EXPERIMENTAL PROCEDURES

Commercial rosins were obtained from gum, wood and tall oil processing plants. Although only one rosin of each type is reported, the gas chromatographic analyses of several samples of each rosin indicated that the neutrals of these samples are typical of the particular rosin. WW grade gum rosin, FF grade wood rosin and refined tall oil rosin were used to isolate the neutral fractions. A wood rosin from *Pinus ponderosa* wood stumps was included for comparative purposes.

The neutral fraction from each rosin was isolated by two methods. The composition of the neutral fraction isolated by either method was qualitatively the same. There were minor quantitative variations in individual components, with more diterpene alcohols present in the fraction

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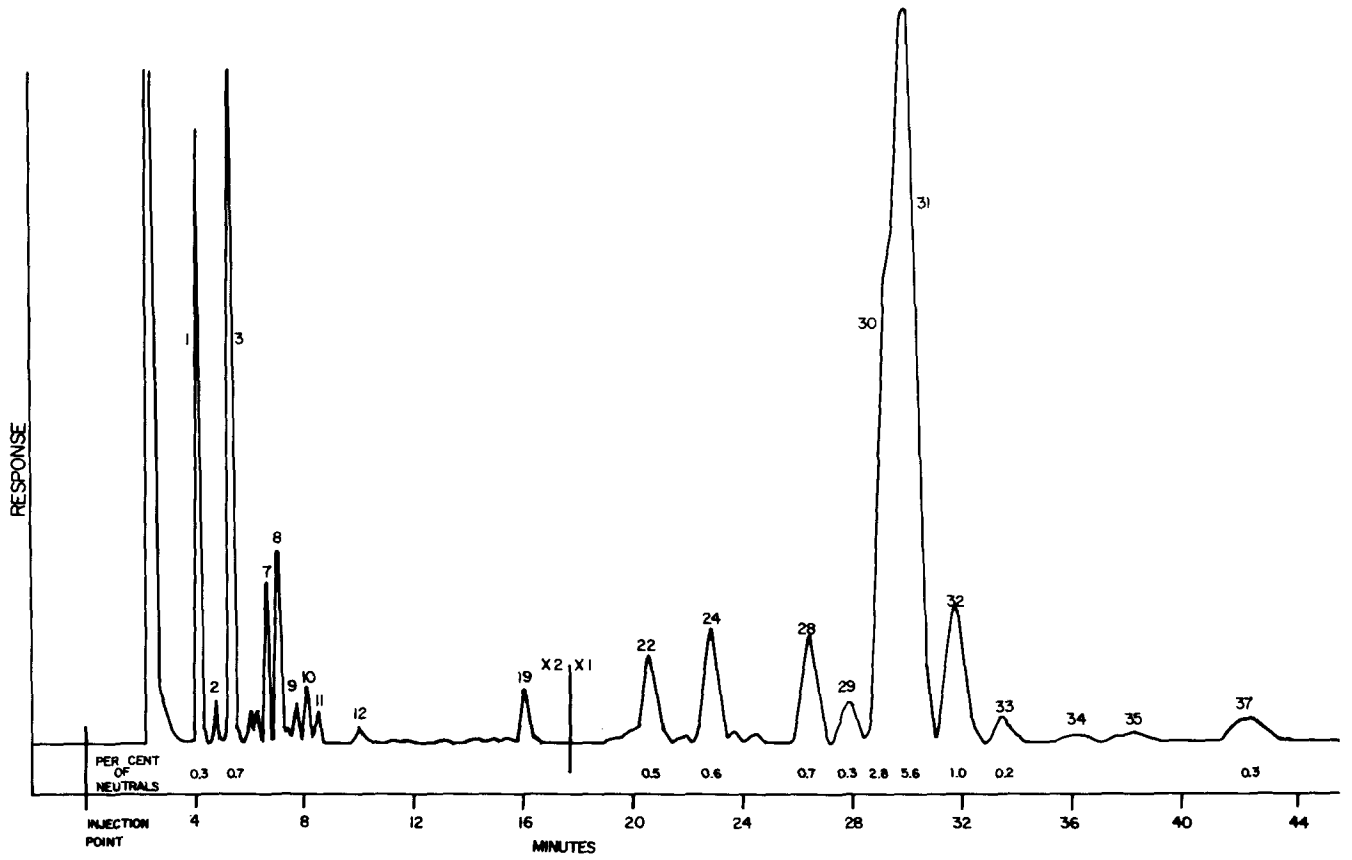

FIG. 1. Chromatogram of monoterpenes in gum rosin neutrals.

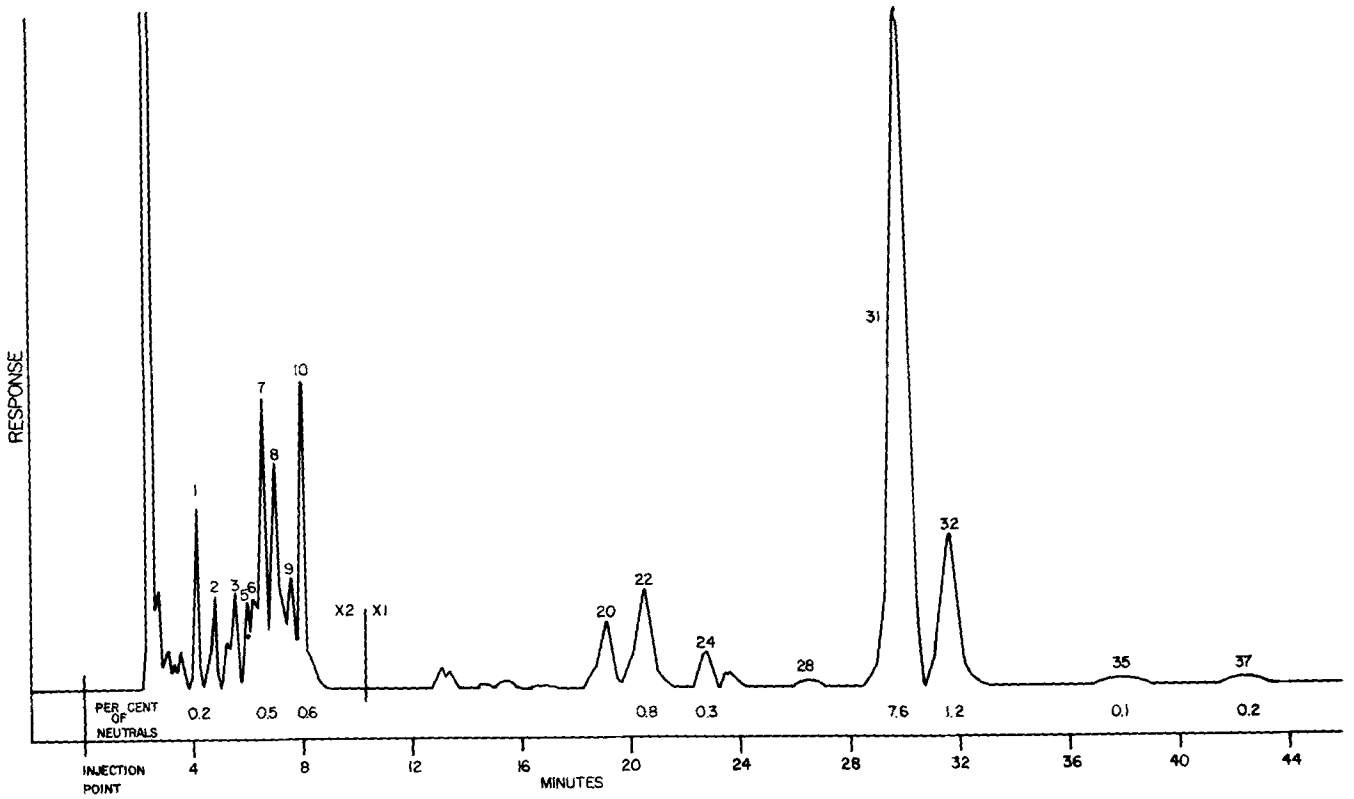

FIG. 2. Chromatogram of monoterpenes in FF wood rosin neutrals.

isolated by method B.

A) Each rosin (100 g) was neutralized with 10% aqueous sodium hydroxide and diluted to 1 liter with water. Ether was added until two layers formed (ca. 1 liter), and the aqueous rosin solution was extracted in a continuous extractor for 25 hr. The ether extract was removed, fresh solvent added, and the extraction continued until no material was extracted during an 8 hr period. The total extraction time was 40 hr. The ether extracts were combined, washed neutral with water, dried, and the

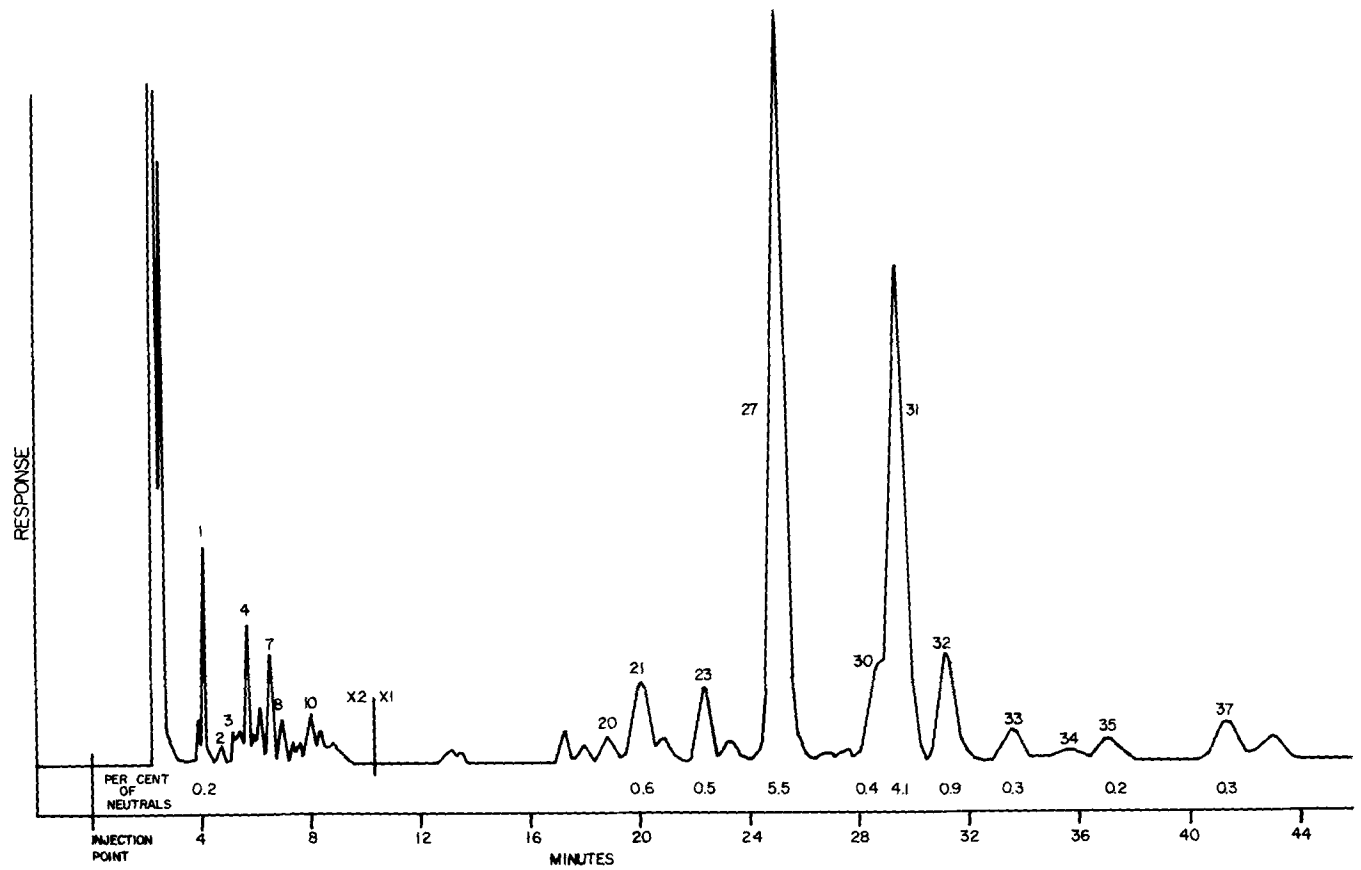

FIG. 3. Chromatogram of monoterpenes in ponderosa wood rosin neutrals.

TABLE I

Diterpenes in Rosin Neutrals

Component[a]	Retention time[b]	Neutral, % Rosin type Gum	Wood[c]	Wood[d]	Tall oil
Pimaradiene	0.47	0.8	1.1	1.2	---
Palustridiene	0.49	1.9	3.0	2.6	---
Dehydroabietane	0.55	1.3	1.2	1.4	---
Abietadiene	0.58	3.1	2.3	3.1	---
Pimarinal	1.00	8.8	4.3	6.2	---
Palustrinal	1.11	4.2	0.5	0.9	---
Isopimarinal	1.22	13.4	9.7	10.5	---
Dehydroabietinal and 3,5-dimethoxystilbene[e]	1.43	3.6	9.1	8.2	---
Palustrinol	1.47	4.1	1.5	1.8	---
Elliotinal	1.67	3.7	1.3	---	---
Abietinal	1.77	4.8	2.5	2.0	---
Dehydroabietinol	1.96	1.6	0.4	1.6	---
Neoabietinal	2.13	1.8	0.5	0.5	---
Pimarinol	2.65	4.1	6.6	8.9	1.5
Sandaracopimarinol	3.02	1.2	5.9	3.7	1.4
Isopimarinol	3.22	7.1	10.7	9.7	12.3
Elliotinol and abietinol[e]	4.15	2.6	3.7	3.5	20.1
β-Sitosterol	4.25	---	---	---	26.4
Neoabietinol	4.84	1.3	1.6	1.1	0.9

[a]Over 50 components were detected by gas chromatography. Only the major components identified are included.

[b]Relative retention times are relative to pimarinal. The total analysis time was ca. 1 hr.

[c]Commercial FF wood rosin.

[d]Wood rosin from *Pinus ponderosa* stumps.

[e]These components were not separated under the conditions used.

solvent removed under reduced pessure. The recovered neutral fractions were pale yellow viscous oils with a pleasant pine aroma. Yields of neutrals were: from gum rosin, 7.5%; FF wood rosin, 10.0%; ponderosa wood rosin, 15.0%; and tall oil rosin, 4.0%.

B) Each rosin (100 g) was dissolved in isooctane and diluted to 1 liter. The insolubles were removed by filtration, and 33 g cyclohexylamine was added in three portions. The precipitated salts were removed by filtration, washed with fresh solvent, and the filtrates combined. The isooctane filtrate was acidified with 3 N phosphoric acid, washed neutral with water, extracted with 2.0% aqueous sodium hydroxide, washed neutral with water, and dried. The solution was filtered and the solvent removed under reduced pressure to give pale yellow viscous oils. The yields were: from gum rosin, 8.0%; FF wood rosin, 10.5%; ponderosa wood rosin, 16%; and tall oil rosin, 4.3%.

Each of the neutral fractions was analyzed on a F&M 700 gas chromatograph equipped with dual columns and flame ionization detector. The monoterpenes and their derivatives were separated on a 12 ft 1/8 in. OD column packed with 20% Carbowax 20M on 80/100 mesh Chromosorb W at 150 C and a flow of 50 ml He/min. The detector and injection port were maintained at 300 C.

The diterpene derivatives were separated on a 15 ft 3/16 in. OD column packed with 5% Versamid 900 on 80/100 mesh Gas Chrom Q at 240 C and a flow of 100 ml of He/min. The detector and injection port were maintained at 300 C.

TABLE II

Rosin Physcial Constants

Rosin type	Neutral, %	Acid number	Softening point, C[a]
Gum	7.5	166	75
Wood[b]	10.0	150	72
Wood[c]	15.0	138	62
Tall oil	4.0	171	78

[a]ASTM Ball & Ring method.

[b]Commercial FF wood rosin.

[c]Wood rosin from ponderosa pine stumps.

Peak areas were measured with a disc integrator. Retention times were measured from the point of injection to the intersection of the tangent of the front side of each peak and the base line. Relative retention times in Table I are relative to pimarinal. Response factors of individual components were determined and used in calculating the per cent of each component. Unidentified components were assigned response factors according to the area of the chromatogram they are in.

The identity of each component was determined by comparison of its relative retention time and IR and UV spectra with those of authentic samples. Many of the gas liquid chromatographic peaks were found to contain more than one component, and the reporting of one component does not necessarily rule out the presence of others.

RESULTS AND DISCUSSION

Figures 1-3 compare the monoterpenes in gum and wood rosin neutrals. The neutral fraction from tall oil rosin did not contain monoterpene components. The major monoterpene components identified from gum and wood rosin neutrals were α-pinene (1); β-pinene (3); limonene (7); β-phellandrene (8); *trans*-dihydro-α-terpineol (22); *cis*-dihydro-α-terpineol (24); longifolene (27); β-terpineol (28); methyl chavicol (estragole) (30); α-terpineol (31); and borneol (32). Minor components that were identified included camphene (2); Δ3-carene (4); α-terpinene (5); α-phellandrene (6); para-cymene (10); terpinolene (11); alloocimene (12); bornyl acetate (23); and caryophyllene (26).

Table I compares the diterpenes found in the neutral fractions from gum, wood and tall oil rosins. The components that were identified include pimaradiene, palustridiene, dehydroabietane, abietadiene, pimarinal, palustrinal,

isopimarinal, dehydroabietinal, elliotinal, abietinal, neoabietinal, 3,5-dimethoxystilbene, palustrinol, dehydroabietinol, pimarinol, sandaracopimarinol, isopimarinol, elliotinol, abietinol, neoabietinol and β-sitosterol.

Approximately 70% of the neutral fractions from gum and wood rosins is volatile enough to pass through the gas chromatograph under the conditions used. The remaining portion appears to be dimeric and polymeric material. The monoterpenes account for 12-15% of the volatiles from gum and wood rosin neutrals; the diterpene hydrocarbons make up 8-12%; and the diterpene aldehydes and alcohols account for 62-83%.

Table II illustrates the affect the neutral fraction has on the acid number and softening point of rosin. The commercial FF wood rosin containing 10% neutrals has an acid number of 150 and softening point of 72 C; while the ponderosa wood rosin containing 15% neutrals has a lower acid number of 138 and softening point of 62 C. These same differences can be seen between the wood and gum rosins, as well as between the gum and tall oil rosins.

The neutral fractions from gum, wood and tall oil rosins were shown to be complex mixtures. Over 70 components were detected in the neutral fractions from gum and wood rosins. These components range from terpenes, terpene alcohols, sesquiterpenes and other terpene derivatives to diterpene hydrocarbons, aldehydes and alcohols. Diterpene alcohols and aldehydes corresponding to all of the major resin acids were detected. Diterpene hydrocarbons corresponding to most of the resin acids were also identified.

The major neutral components from all three types of rosin are diterpene aldehydes and alcohols. Gum and wood rosin neutral fractions contain monoterpenes and diterpene hydrocarbons that are not present in the neutral fraction from tall oil rosin. Tall oil rosin neutrals contain β-sitosterol and possibly other steroidal compounds not found in gum or wood rosin neutral fractions. 3,5-Dimethoxystilbene was found in the neutral fractions from gum and wood rosin after the neutrals were saponified and the unsaponified portion examined.

The presence of primary diterpene alcohols in rosin neutrals explains the loss of acid number that occurs on heating rosin below a temperature where decarboxylation occurs. They apparently react with the resin acids to form esters.

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