Acidic Composition of Oleoresins and Rosins

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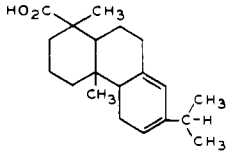
The naval stores industry of today produces three types of rosin—gum rosin, wood rosin, and tall oil rosin. The production pattern of the last few years places each rosin in an important commercial position, as figures for 1955-56 indicate: The wood naval stores industry produced 712,000,000 pounds of rosin, the gum naval stores produced 236,000,000 pounds, and crude tall oil production, which amounted to 600,000,000 pounds, contained resin acids equivalent to about 250,000,000 pounds of rosin.

The largest single use for rosin, paper size, consumes approximately 230,000,000 pounds per year. Conversion of rosin into ester gums, synthetic resins, chemicals, and pharmaceuticals accounts for about 320,000,000 pounds per year. Other uses are in adhesives, plastics, floor coverings, paints, varnishes, lacquers, rubber, and soaps.

These varied uses make it important to understand the composition of rosin and the reactions of its components. All three types of rosin are composed of about 90% acidic material, primarily monobasic acids having the empirical formula $C_{20}H_{30}O_2$. Work on the isolation and characterization of individual acids in pine oleoresin and rosin dates back to 1824. Since then, levopimaric acid has been isolated from oleoresins and six other pure resin acids have been isolated from both oleoresins and rosins without subjecting the starting material to drastic heat or acid conditions.

Dihydro- and tetrahydroresin acids have been isolated from rosin only after acid or heat treatment of the rosin.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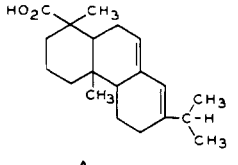
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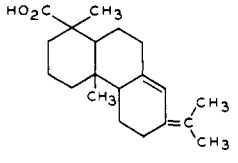
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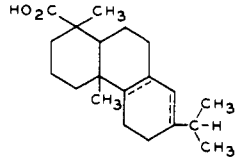
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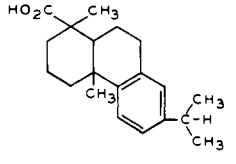
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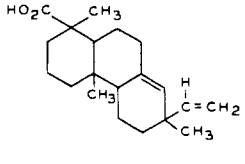
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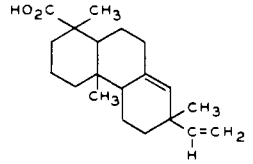
ISO-DEXTROPIMARIC ACID

The resin acids may be classified in two types—abietic and pimaric. The abietic-type group includes acids that form retene on dehydrogenation—levopimaric, *l*-abietic, neoabietic, palustric, and dehydroabietic acids, and their hydrogenated derivatives. The pimaric-type acids are dextropimaric and isodextroprimaric, which form pimanthrene on dehydrogenation.

The acidic composition of a rosin is governed by the conditions to which it is subjected during processing and conversion into other chemical derivatives. In general, high temperatures, prolonged heating, and treatment with acid decrease both the heterogeneity and chemical reactivity of rosin. Heterogeneity in this sense means a mixture of small amounts of a large number of acids. Any rosin that contains more than about 30% of any one acid is not desirable, as that acid may begin to crystallize and, with its crystallization, bring down other resin acids. The rosin then is no longer a resin but a semicrystalline product containing a mixture of crystalline acids suspended in a resin. In most uses of rosin, a resinous product containing small amounts of several acids is desirable.

The acidic composition in turn governs the chemical reactivity of the resin. In reactions involving the conjugated double bond system levopimaric acid is more reactive than palustric, *l*-abietic, or neoabietic acids. On the other hand, *l*-abietic acid is the most sensitive to autoxidation. These differences make it desirable for rosin producers and consumers to know the ratio of resin acids present in rosin.

Throughout the years elucidation of the composition of rosin has been hindered by two factors—inability to separate the pure resin acids by ordinary chemical means because of similarity in structure, and ease with which some of the abietic-type acids in oleoresin and rosin isomerize on treatment with heat or acids.

A chromatographic technique (*2*) partially divides a small sample of oleoresin or rosin into its components without subjecting it to strong chemical treatment which could change the ratio of the acids present. This technique separates the acids into groups, so that a combination of the chromatographic data and the ultraviolet absorption characteristics of the conjugated-diene acids in each group produces, for the first time, a fairly comprehensive picture of the composition of pine oleoresin and rosin.

The chromatographic procedure used has been described

Table I. Acids Eluted in Chromatographic Groups

Group	Eluent Range, Ml.	Elution of Known Acid Mixtures	Acids Identified in Oleoresin and Rosin Samples[a]
1	10–260	C_{16}, C_{18} saturated fatty acids	
		Dihydro acids	None[b]
		Tetrahydro acids	
2	270–310	Palustric	Palustric
		Dextropimaric	Dextropimaric
		Isodextropimaric	Isodextropimaric
3	320–420	*l*-Abietic	*l*-Abietic
		Dextropimaric	Dextropimaric
		Isodextropimaric	Isodextropimaric
		Levopimaric	Levopimaric[c]
		Oleic	
4	430–600	Neoabietic	Neoabietic
5	610–800	Dehydroabietic	Dehydroabietic
6	Beyond 800		None[d]

[a] Some acids of each group trail into succeeding group.
[b] From ultraviolet data, caribeic (*1*) and other conjugated acids may be in this group.
[c] Found only in oleoresin samples.
[d] Most polar constituents should be in this group.

Table II. Chromatographic and Ultraviolet Absorption Data on Pine Oleoresins and Gum Rosins

Group		Longleaf Oleoresin	Longleaf Rosin	Slash Oleoresin	Slash Rosin	Pine Oleoresin	Gum Rosin
1	%	0	0	4	4	4	4
2	%	12	23	10	17	12	20
	$[\alpha]_D$	+66°	+68°	+71°	+63°	+67°	+57°
	α at 266 mμ	24.4	24.0	24.3	24.3	22.6	21.6
3	%	57	43	50	45	51	43
	$[\alpha]_D$	−136°	−55°	−106°	−59°	−131°	−59°
	α at 242 mμ	15.6	38.8	14.6	29.7	14.0	33.5
	α at 272 mμ	10.0		8.4		7.9	
4	%	16	17	17	20	13	18
	$[\alpha]_D$	+120°	+127°	+114°	+129°	+100°	+141°
	α at 251 mμ	76.4	72.0	71.8	71.0	70.6	79.0
5	%	7	10	5	6	5	7
	$[\alpha]_D$	+36°	+34°		+31°	+44°	+36°
	α at 284–6 mμ	2.4	7.5	1.6	10.9	2.1	6.5
	α at 276 mμ	5.1	11.6	4.5	16.0	5.0	10.4
	α at 268 mμ	5.4	10.6	4.9	13.8	5.0	10.2
6	%	6	5	11	6	10	7

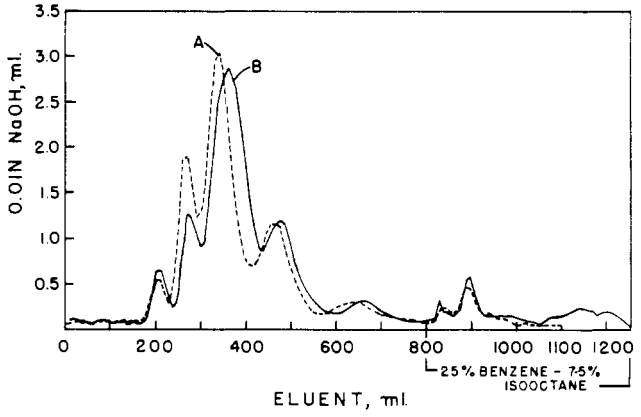

Figure 1. Chromatogram of slash oleoresin and rosin

A. Slash rosin
B. Slash oleoresin

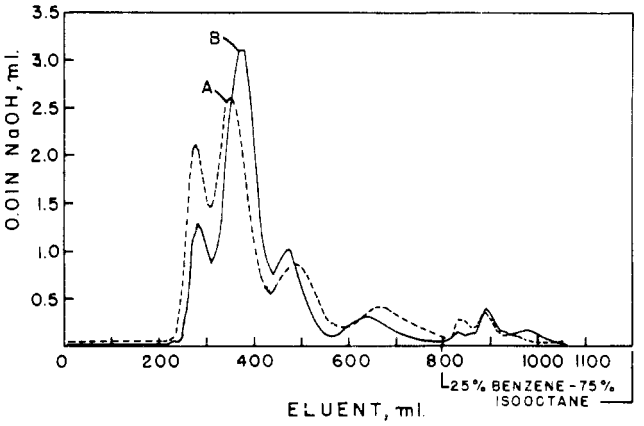

Figure 2. Chromatogram of longleaf oleoresin and rosin

A. Longleaf rosin
B. Longleaf oleoresin

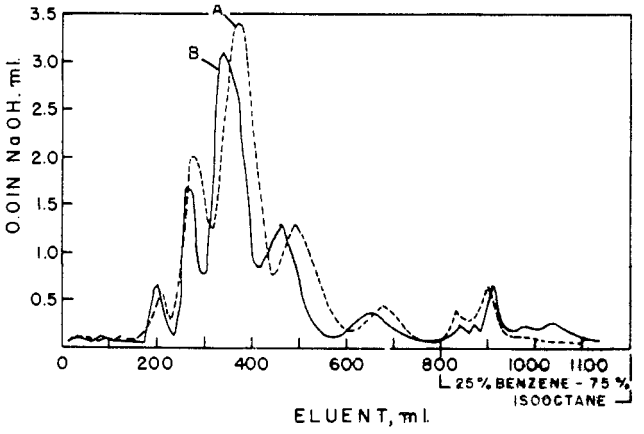

Figure 3. Chromatogram of pine oleoresin and gum rosin

A. Gum rosin
B. Pine oleoresin

in detail (*2, 3*). The technique divides the resin acids in oleoresins and rosins into six groups, which in some cases consist of several small peaks especially groups 1 and 6. The data in Table I were compiled from chromatograms of individual acids, mixtures of pure acids, and chromatograms of oleoresin and rosin samples.

After all the fractions of the oleoresin and rosin chromatograms were titrated, the fractions comprising each peak were combined, acidified with 0.2*N* acetic acid, washed neutral, and dried over sodium sulfate. An attempt was made to precipitate the resin acids in each group with cyclohexylamine. Groups 2 through 5, and in some samples group 6, formed insoluble salts. The ultraviolet absorption spectrum and the specific rotation (in ethyl alcohol) of these salts were obtained. Both the specific extinction coefficients, α, and the specific rotations were calculated for the acid rather than the salt. Where an insoluble cyclohexylamine salt did not form, because of either the nature or the smallness of the sample, the ultraviolet absorption spectrum was not reported because trace amounts of furfuryl alcohol remaining in the iso-octane solution interfered with the resin acid absorption between 220 and 320 mμ.

The samples included in this study are longleaf oleoresin, longleaf rosin, slash oleoresin, slash rosin, pine oleoresin, gum rosin, the resin acids extracted from a fat pine stump, two pale wood rosins, the resin acids extracted from a living slash pine tree, the resin acids extracted from black liquor soap, and a distilled tall oil rosin.

PINE OLEORESINS AND GUM ROSINS

The raw material of the gum naval stores industry is the oleoresins from *Pinus palustris* (longleaf pine) and *Pinus elliotti* (slash pine). For this work the pure slash and longleaf rosins were obtained by laboratory distillation of the oleoresins. The pine oleoresin and gum rosin were obtained from a central processing plant.

Inspection of the chromatographic curves and percentages of acids in the various groups indicated certain similarities and differences in the oleoresins and gum rosins (Table II and Figures 1 to 3).

By comparing the ultraviolet spectra of groups 2 to 5 with the spectra of the pure resin acids it was possible to calcu-

late the maximum percentage of the conjugated acids present in each group. This value, multiplied by the chromatographic percentage of its respective group, gave an approximation (±2%) of the maximum amount of the acids in the oleoresins and rosins which have characteristic ultraviolet absorption (Table III).

Table III. Composition of Pine Oleoresins and Gum Rosins

	Max. % of Resin Acids Having Characteristic Ultraviolet Absorption				
	Palustric	Levopimaric	*l*-Abietic	Neoabietic	Dehydroabietic
Longleaf oleoresin	11	31	10	14	7
Slash oleoresin	9	24	10	15	5
Pine oleoresin	9	25	10	15	5
Longleaf rosin	18	0	26	14	8
Slash rosin	13	0	23	16	5
Gum rosin	14	0	20	18	6

Oleoresins. The slash and commercial oleoresins contained 4% of an acid or group of acids not present in longleaf oleoresin (Table II, group 1). The percentage of acids in the palustric acid group (group 2) of all three oleoresins was approximately the same. Group 3, which in the oleoresins is composed of levopimaric, *l*-abietic, isodextropimaric, and dextropimaric acids, contained 57% of the acids in longleaf gum but only about 50% in slash and pine oleoresin. The higher value for longleaf gum is due to higher amounts of levopimaric acid in the oleoresin of this species. The group containing predominantly neoabietic acid (group 4) was approximately the same for all three oleoresins. In all cases the group containing dehydroabietic acid was contaminated with 5 to 10% neoabietic acid. The ultraviolet absorption spectrum of the acids in this group showed the presence of another resin acid which has maximum characteristic absorption at 284 to 286 mμ. The shape of the chromatographic curve of group 6 of the oleoresins is similar, but percentages vary between 6 and 11% for the different samples. Commercial samples of oleoresin fall between the pure slash and pure longleaf samples, depending on the species predominating in the location of collection.

Gum Rosins. Previous work on the thermal isomerization of levopimaric acid (*3*) has shown that, at the processing time and temperature for pine gum, the levopimaric acid isomerizes to a mixture which contains approximately 34% palustric acid, 52% *l*-abietic acid, and 14% neoabietic acid. This isomerization accounts for the major changes in composition that occur when the oleoresin is processed into rosin. As a result, rosin contains essentially no levopimaric acid and more palustric, *l*-abietic, and neoabietic acids than the oleoresin.

The effects of this isomerization are exhibited by the changes in the chromatographic percentages and ultraviolet absorption spectra of groups 2, 3, and 4 in longleaf, slash, and gum rosin. As in the oleoresins, 4% of the total acids in slash rosin and gum rosin was in group 1. The palustric group in all these rosins was 17 to 23%, an increase of 7 to 11% during processing. The higher value for the palustric acid group in longleaf rosin is the result of the higher levopimaric acid content of the oleoresin. Group 3, which contains *l*-abietic, dextropimaric, and isodextropimaric acids, when compared with the oleoresins, has decreased chromatographic percentages due to the isomerization of the levopimaric acid to palustric and neoabietic acids. The ultraviolet absorption data showed an increase in the *l*-abietic content of the rosins, likewise caused by isomerization of levopimaric acid to *l*-abietic acid. Group 4 also showed a slight increase in neoabietic acid content, in accordance with the isomerization of levopimaric acid during processing. The chromatographic percentages and ultraviolet absorption spectra of group 5 indicated no major change in the dehydroabietic acid content during conversion of the oleoresins to rosins. In the rosins the chromatographic curve for group 6 is similar in shape to the first portion of group 6 in the oleoresin curve; however, the most highly polar acids present in the oleoresins seemed to be absent in the rosins. This was also evidenced by a slight decrease in the chromatographic percentages for this group in the rosins.

The percentages of dextropimaric and isodextropimaric acids present in the oleoresins and rosins have not been estimated, because the chromatographic technique does not separate these acids from the conjugated acids in groups 2 and 3. A chromatogram of pure dextropimaric and isodextropimaric acids indicated that they are eluted in groups 2 and 3—predominantly in group 3. Infrared curves of groups 2 and 3 show the presence of these acids, as the vinyl group is readily discerned. As dextropimaric and isodextropimaric acids are stable to heat and acids, their percentage in the oleoresins and rosins should depend on the characteristics of the species and should not change when the oleoresin is processed into rosin.

Hence, when pine oleoresin is processed into gum rosin the major changes in composition are a result of the thermal instability of levopimaric acid. The isomerization results in a more equal percentage distribution of the conjugated-diene acids in the rosin and a change in the physical characteristics of the semicrystalline oleoresin into a clear, noncrystalline rosin.

WOOD ROSIN

Pine stumps that have aged in the earth until the bark and sapwood have disappeared are extracted with a hydrocarbon solvent to recover the volatile oils and resins. Pale wood rosin may be obtained from the resinous fraction by selective solvent refining with furfural, or refining with fuller's earth or other activated adsorbents.

Table IV. Chromatographic and Ultraviolet Absorption Data on Wood Rosins

Group		Resin Acids from Fat Pine Stumps	Wood Rosin A	Wood Rosin B
1	%	0	2[a]	1[a]
2	%	12	17	16
	$[\alpha]_D$		+73°	+72°
	α at 266 mμ		24.6	24.3
3	%	60	57	60
	$[\alpha]_D$		−54°	−52°
	α at 242 mμ		52.8	48.1
4	%	12	13	11
	$[\alpha]_D$		+134°	+138°
	α at 251 mμ		72.9	74.0
5	%	9	9	11
	$[\alpha]_D$		+20°	+36°
	α at 284–6 mμ		2.1	0.9
	α at 276 mμ		4.8	4.8
	α at 267 mμ		5.3	5.2
	α at 251 mμ		6.4	6.4
	α at 241 mμ		6.4	6.4
6	%	6	2	0

[a] Eluted in several small peaks.

When the data from the chromatographic and ultraviolet adsorption examination of two samples of pale wood rosin (Table IV, Figure 4) were compared to the data on gum rosin, several distinct differences were noted: the presence of small amounts of the acids comprising group 1 in slash rosin and gum rosin, an increase in the concentration of *l*-abietic acid to approximately twice the amount present in gum rosin, a 4 to 5% decrease in neoabietic acid content, a 3 to 4% increase in the group containing dehydroabietic

acid (group 5), and a decrease in the amount of polar acids (group 6).

To determine whether these differences were due to the processing conditions for wood rosins or changes during aging of the stumps, the composition of resin acids from fat pine stumps was investigated. The wood was extracted with iso-octane, and the resin acids were precipitated as the cyclohexylamine salts, converted to the acids, and chromatographed. Group 2 contained about 5% less acids than

Table V. Composition of Wood Rosins

	Max. % of Resin Acids Having Characteristic Ultraviolet Absorption				
	Palustric	Levopimaric	*l*-Abietic	Neoabietic	Dehydroabietic
Wood rosin A	13	0	42	11	8
Wood rosin B	12	0	41	9	10

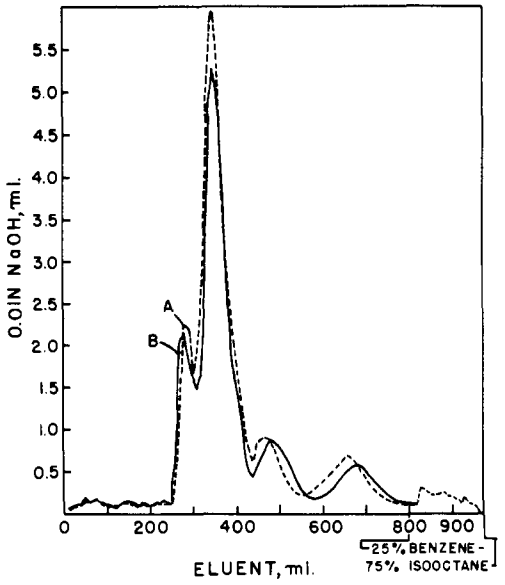

Figure 4. Chromatogram of wood rosins

A. Wood rosin A
B. Wood rosin B

the wood rosin samples. The percentage of the acids in groups 3 through 5 was similar to those in both samples of wood rosin. Group 6 contained 7% polar acids which had a chromatographic curve similar to the curve of group 6 in gum rosin. These results indicated that changes during the aging of the stumps rather than processing conditions are largely responsible for the percentages of the various resin acids observed in wood rosin. The difference in the amount of polar acids in wood rosin and the resin acids extracted from pine stumps indicated that the polar acids are removed during refining.

The same procedure was followed to obtain the maximum percentages of the acids in the wood rosins which have characteristic ultraviolet absorption (Table V).

TALL OIL ROSIN

Tall oil rosin is a product of the sulfate or kraft paper process. During digestion of the wood chips with alkali, the fatty and resin acids form a soap. This black liquor soap, on acidification, yields crude tall oil, which can be refined, and separated into fatty acids and rosin.

To trace the changes during production of tall oil rosin, the composition of the resin acids in three stages of the process were investigated by chromatography and ultra-

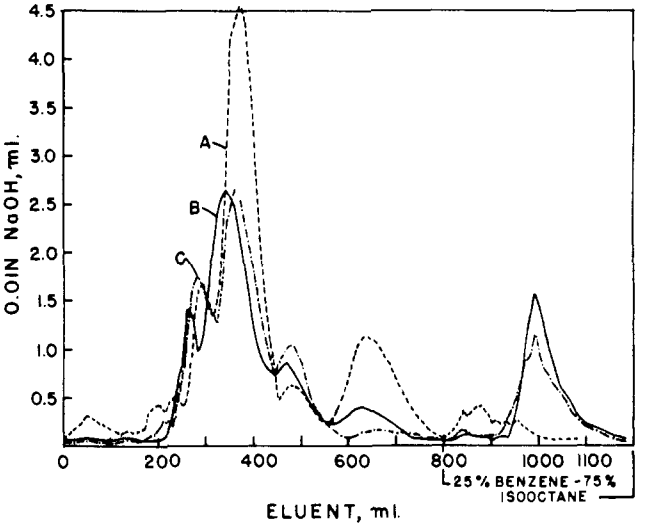

Figure 5. Chromatogram of intermediates and products of sulfate process

A. Tall oil rosin
B. Resin acids from black liquor soap
C. Resin acids from slash pine wood

Table VI. Chromatographic and Ultraviolet Absorption Data on Intermediates of Sulfate Process

Group		Resin Acids from Slash Pine Wood		Resin Acids from Black Liquor Soap	Tall Oil Rosin
1	%	1[a]	1[b]	0	6[c]
2	%	18	10	9	10
	$[\alpha]_D$	+52°	+74°	+73°	+51°
	α at 266 mμ	20.4	24.7	28.8	21.6
3	%	41	57	49	52
	$[\alpha]_D$	−91°	−68°	−66°	−68°
	α at 242 mμ	22.5	15.2	27.5	55.9
	α at 272 mμ	5.2	7.7	...	...
4	%	14	19	12	7
	$[\alpha]_D$	+126°	+93°	+116°	...
	α at 251 mμ	77.4	67.6	69.2	21.8
5	%	3	2	6	20
	$[\alpha]_D$	+47°	...	+47°	+56°
	α at 284-6 mμ	1.6	...	1.4	0.8
	α at 276 mμ	4.2	4.5	4.5	2.7
	α at 268 mμ	...	...	4.9	2.8
	α at 252 mμ	7.5	7.6	5.3	2.2
	α at 242 mμ	7.2	6.6	5.0	2.1
6	%	21	11	25	4
	$[\alpha]_D$	−8°	...	−12°	...
	α at 242 mμ	27.9	...	31.5	...
	α at 250 mμ	26.9	...	26.5	...

[a]Wood shaved before extraction.
[b]2 × 3 inch chunks of wood extracted under N_2 blanket.
[c]Eluted in four peaks between 0 and 250 ml.

violet absorption analysis of each group of acids from the chromatograms (Table VI, Figure 5). Shavings of wood from a living slash pine were extracted with iso-octane, followed by precipitation of the resin acids with cyclohexylamine. The amine salt was suspended in ether and acidified with 3*N* acetic acid. In comparing the composition of these acids with the acids from slash oleoresin, two striking differences were noted: a smaller amount of levopimaric acid in the wood extract, and a larger amount of highly polar acidic material (21%) in group 6 (not the same as the polar material in the oleoresin). It formed a crystalline, insoluble cyclohexylamine salt in iso-octane, and had a negative specific rotation, characteristic ultraviolet absorption at 241 and 250 mμ, and infrared absorption at 2.93 microns, indicating the presence of an OH group. It could be separated from the other resin acids extracted from the

slash pine tree by virtue of its solubility in 2% aqueous sodium bicarbonate solution. To determine whether the acidic material in group 6 could have been formed by oxidation during the shaving of the wood, another sample of resin acids was obtained by extracting 2 × 3 inch chunks of wood under a blanket of nitrogen. Group 6 from this sample contained only 11% of the acids in the sample, and did not form an insoluble cyclohexylamine salt. The remaining groups of acids in this sample were similar in composition to slash oleoresin. These data indicate that oxidation occurs during the chipping of wood.

The composition of the resin acids obtained from black liquor soap was then investigated. The soap was acidified with 3*N* acetic acid and the resin acid–fatty acid mixture extracted with ether. Dilution of the ether solution with acetone and addition of cyclohexylamine precipitated the resin acids, while the fatty acids remained in solution. The cyclohexylamine salts were converted into the acids with 3*N* acetic acid. These acids contained no levopimaric acid and amounts of *l*-abietic acid greater than those observed in the slash pine wood extract—indicating that some isomerization occurred during digestion of the wood. Group 6 of the chromatogram contained approximately 25% of a strongly polar acidic material similar to the material found in the shaved slash pine wood extract.

Investigation of a distilled tall oil rosin demonstrated some of the changes that occur during acidification of the black liquor soap and separation of the tall oil into fatty acids and rosin. Approximately 6% of the acids in the tall oil rosin was eluted in group 1. The palustric acid group was similar to that of black liquor soap, while the *l*-abietic acid content increased approximately 12%. The percentage of acids eluted in the group containing neoabietic acid (group 4) was similar to that in the black liquor soap; however, the ultraviolet absorption spectrum indicated that neoabietic acid represented only 14% of the group. Group 5 showed an increase in dehydroabietic acid content from 6% in the black liquor soap to 17% in tall oil rosin. Group 6 contained only 4% polar acids, which did not correspond to the polar material isolated from the acids extracted from shaved slash pine wood and black liquor soap.

Calculations similar to those for the pine oleoresins and gum rosins and the wood rosins resulted in estimation of the maximum percentages of the known conjugated-diene resin acids present in the intermediates and products of the sulfate process (Table VII).

Table VII. Composition of Intermediates and Products of Sulfate Process

	Max. % of Known Resin Acids Having Characteristic Ultraviolet Absorption				
	Palustric	Levopimaric	*l*-Abietic	Neoabietic	Dehydroabietic
Slash pine wood	12	14	14	12	3
Black liquor soap	7	0	27	9	6
Tall oil rosin	7	0	39	4	17

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Long-Chain Phosphorus Compounds as Low Temperature Plasticizers for Vinyl Chloride Polymers

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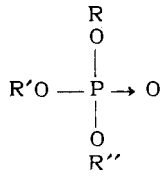
Research on plasticizers derivable from fats being conducted in this laboratory has been directed mainly toward the correlation of structure with compatibility and certain other important characteristics desired in a plasticizer (low temperature properties, lack of volatility, etc.). The authors have described the effect of introducing the oxirane (*6*) or acetoxy (or higher acyloxy) (*4*) group into fatty acid esters. These groups, singly or together, are effective in compatibilizing long-chain compounds with vinyl chloride polymers, and compositions with outstanding low temperature properties are obtained.

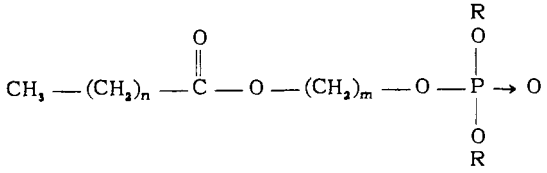
Groups containing the phosphorus atom are also known to impart useful properties to plasticizers, and a number of phosphorus-containing plasticizers are commercially available. None of these, however, contains long chain or other structures derived from fats.

For the past 4 years the authors have been systematically preparing long-chain phosphorus compounds of various types (*1–3*): trialkyl phosphates (I), dialkyl acyloxyalkyl phosphates (II), dialkyl acyloxyalkylphosphonates (III), alkyl (α-dialkylphosphono)alkanoates (IV), and some miscellaneous compounds.



(I)

R = R′ = R″ = Dodecyl, octadecyl or oleyl
R = Dodecyl or oleyl, and R′ = R″ = ethyl



(II)

n = 10, *m* = 2–4, and R = ethyl or *n*-butyl

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