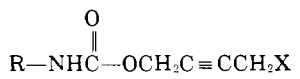
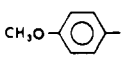
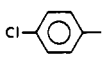
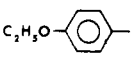
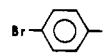
Table II. Characterization of Carbamates and Carbanilates



Compound	R	X	M.P., °C.	Yield, %	Analysis
4-Iodo-2-butynyl *N*-methylcarbamate	CH_3—	—I	37–40	22	Calcd. C, 28.4; H, 3.2; N, 5.5 Found C, 28.3; H, 3.0; N, 5.3
4-Iodo-2-butynyl *N*-(*n*-octyl)carbamate	n-C_8H_{17}—	—I	47.5–51	51	Calcd. C, 44.5; H, 6.3; N, 4.0 Found C, 44.0; H, 6.0; N, 4.0
4-Iodo-2-butynyl *p*-methoxycarbanilate		—I	93.5–95.5[a]	32	Calcd. C, 41.7; H, 3.5; N, 4.1 Found C, 41.9; H, 3.4; N, 3.9
4-Iodo-2-butynyl *p*-chlorocarbanilate		—I	133–133.5[a]	32	Calcd. C, 37.8; H, 2.6; N, 4.0 Found C, 38.1; H, 2.6; N, 3.8
4-Iodo-2-butynyl 2′,5′-dichlorocarbanilate		—I	60–62[a]	17	Calcd. C, 34.4; H, 2.1; N, 3.6 Found C, 33.9; H, 1.7; N, 3.5
4-Thiocyanato-2-butynyl *p*-ethoxycarbanilate		—SCN	86–89[b]	38	Calcd. C, 57.9; H, 4.9; N, 9.6 Found C, 57.8; H, 4.6; N, 9.6
4-Thiocyanato-2-butynyl *p*-bromocarbanilate		—SCN	128–129	12	Calcd. C, 44.3; H, 2.8; N, 8.6 Found C, 44.3; H, 2.8; N, 8.4

[a] Recrystallized from ethanol. [b] Recrystallized from petroleum ether.

ACKNOWLEDGMENT

The authors acknowledge the support of the Department of the Army at Fort Detrick. Elemental analyses were performed by Carol K. Fitz, Needham Heights, Mass.

LITERATURE CITED

(1) Bailey, W.J., Fujiwara, E., *J. Am. Chem. Soc.* **77**, 165 (1955).
(2) Hopkins, T.R., U. S. Patent **3,127,408** (March 31, 1964).
(3) Hopkins, T.R., Neighbors, R.P., Strickler, P.D., Phillips, L.V., *J. Org. Chem.* **24**, 2040 (1959).

RECEIVED for review August 15, 1966. Accepted December 2, 1966.

Resin Acid Composition of Pine Oleoresins

N. MASON JOYE, Jr., and RAY V. LAWRENCE
Naval Stores Laboratory, Olustee, Fla.

The resin acid composition of the oleoresins and rosins from various species of pines is reported. The data indicate that the source of some oleoresins can be identified by their composition.

THE USE of gas chromatography for the analysis of resin acids was first reported in 1959 by Hudy (*5*). Gas chromatography was used in this work to analyze the acid fraction of pine oleoresins and rosin. The resin acid composition varies considerably from one species to another, and proper selection of the source of oleoresin or rosin can substantially increase the yield of desired acids in work involving the isolation of pure resin acids. From Tables I and II, the pine oleoresin or rosin from which a certain resin acid can best be isolated can be determined. For example, French rosin has twice as much pimaric acid as American rosin, and Greek rosin contains none at all. Isopimaric acid accounts for 21% of the acids in slash pine oleoresin (*Pinus elliottii*) but only 10% of the acids present in longleaf oleoresin (*Pinus palustris*) and only a trace in loblolly oleoresin (*Pinus taeda*).

Table III lists the physical constants of the resin acids and their methyl esters that were studied in this work.

Table I. Composition of Pine Oleoresins and Rosins

Samples	Rel. Ret. Time[a]											
	$\Delta^{8(9)}$-Isopimaric 1.31	Elliotinoic (8) 1.42	Pimaric 1.47	Sandaracopimaric 1.59	Levopimaric and Palustric[b] 1.78	Isopimaric 1.93	Unidentified 2.08	Dehydroabietic 2.19	Abietic 2.53	Neoabietic 2.89	Acid Number[c]	Resin Acids Accounted for, %[d]
Oleoresin	Per Cent of Acid in Acid Fraction[e]											
P. elliottii var. *elliottii*	T[f]	3.1	5.1	1.8	37	21	0.9	3.7	9.7	16	131	95
P. elliottii var. *densa*	T	3.1	3.8	1.9	38	21	0.9	3.7	12	16	123	102
P. palustris	T	0	5.4	1.1	52	10	0	8.3	9.4	13	115	89
P. taeda	T	0	8.7	2.2	64	T	0.9	6.3	8.6	9.5	145	100
P. ponderosa	0.	0	7.6	2.9	40	15	2.9	8.2	11	11	139	88
P. serotina	0	0	4.6	2.9	42	12	0	17	12	8.8	127	94
P. halepensis	0	0	0	1.2	39	10	0	1.5	37	9.7	123	98
P. brutia	0	0	0	1.2	44	10	0	2.5	32	10	140	100
P. pinaster	0.2	0	8.0	2.0	39	12	0	4.2	14	18	115	105
P. strobus	1.0	0.7	4.4	1.3	16	28	0	1.9	34	13	125	102
P. rigida	0	0	4.6	1.3	56	6.7	0	12	7.9	12	133	75
P. caribaea	0	0	4.2	2.2	49	8.0	0	8.6	10	16	139	102
P. peuce	2.8	0	1.8	1.0	12	32	0	0.8	35	14	136	97
Rosin												
P. elliottii var. *elliottii*	T	3.4	5.5	1.8	25	23	T	7.2	19	16	161	100
P. elliottii var. *densa*	T	3.0	4.6	1.3	20	21	0	6.0	28	16	163	101
P. palustris	T	0	4.8	1.6	35	16	0	8.6	18	15	162	98
P. taeda	T	0	5.4	0.9	10	0.9	0	8.1	69	4.7	181	92
P. ponderosa	0	0	9.3	1.7	27	12	0	14	22	13	169	95
P. halepensis	0	0	0	1.6	31	8.9	0	3.6	45	11	171	93
P. brutia	0	0	0	1.4	32	10	0	4.8	40	12	178	87
P. pinaster	0	0	8.9	2.0	26	9.7	0.4	5.7	26	19	172	97
P. caribaea	0	0	6.9	2.3	27	18	0.8	9.0	19	17	175	102
P. edulis	55	1.3	0	3.5	5.3	5.7	0	2.2	21	5.4	160	96

[a] Retention times are calculated relative to the internal standard (1.00). [b] Methyl levopimarate and methyl palustrate are not separated and in pine gum samples the percentages in this column represent the total of the two esters. [c] Acid numbers were determined by using the tetramethylammonium hydroxide titration values. [d] Portion of sample eluted in acid fraction—relative retention time 1.00 to 2.89 divided by total acids present (as calculated from acid number of sample). [e] Acid fraction is that part eluted between relative retention time 1.00 and 2.89. [f] Indicates trace amounts present in sample.

Table II. Composition of Commercial Rosins

Samples	Rel. Ret. Time[a]											
	$\Delta^{8,9}$-Isopimaric 1.31	Elliotinoic (8) 1.42	Pimaric 1.47	Sandaracopimaric 1.59	Palustric[b] 1.78	Isopimaric 1.93	Unidentified 2.08	Dehydroabietic 2.19	Abietic 2.53	Neoabietic 2.89	Acid number[c]	Acids Accounted for, %[d]
Rosin	Per Cent of Acid in Acid Fraction[e]											
American (gum rosin)[f]	0.6	2.8	5.1	1.8	25	17	0.9	5.7	22	20	163	100
Burmese	0	0	7.9	3.0	44	8.3	1.6	6.0	30	2.2	165	102
Chinese	0	0	9.2	2.7	22	1.5	0	4.3	44	15	163	102
French	1.4	0.3	10	2.2	22	7.0	0	4.9	36	17	173	97
Greek	0.7	0	0	1.9	14	11	0	4.5	50	13	159	96
Honduran	0	0	9.6	2.2	21	17	0.5	12	22	15	171	91
Indian	0	0	9.2	1.5	11	20	0	2.0	38	18	161	96
Portuguese	0	0.7	8.8	1.9	30	5.3	0	5.1	32	16	167	89
Russian	0.5	0	7.8	2.4	27	5.6	0	5.3	35	17	174	98
Spanish	0.6	0	8.7	1.5	27	0	0	1.9	36	24	158	93
Tall Oil 1	1.0	1.1	0.6	1.0	14	7.7	5.2	29	37	3.8	173	99
Tall Oil 2	4.4	3.3	1.7	1.6	9.9	15	5.1	29	27	5.3	171	96
Turkish	0.2	0	0	1.3	24	13	0	5.1	41	15	173	98
S. D. Wood 1	0.9	0	5.8	0.8	7.1	12	0	15	59	0	168	97
S. D. Wood 2	0	0	7.4	1.8	18	14	0	11	39	9.6	172	92

[a] Retention times are calculated relative to the internal standard (1.00). [b] Gum rosin usually contains less than 3% levopimaric acid. [c] Acid numbers were determined by using the tetramethylammonium hydroxide titration values. [d] Portion of sample eluted in acid fraction (relative retention time 1.00 to 2.89) divided by total acids present (as calculated from acid number of sample). [e] Acid fraction is that part eluted between relative retention time 1.00 and 2.89. [f] All rosin samples except tall oil and S. D. Wood are gum rosins.

Table III. Resin Acids and Methyl Esters

Sample	M.P., °C.	$[\alpha]_D^{25}$ 2% in 95% EtOH	EtOH λ, mμ	ε
$\Delta^{8(9)}$-Isopimaric acid	106–107	+113	...	...
Methyl $\Delta^{8(9)}$-isopimarate	68–70	+118	...	...
Elliotinoic acid (*8*)	...	+40	232	29,000
Methyl elliotinoate	105–106	+48	232	27,800
Pimaric acid	217–219	+73	...	...
Methyl pimarate	68–69	+72	...	...
Sandaracopimaric acid	173–174	−20	...	...
Methyl sandaracopimarate	68–69	−21	...	...
Palustric acid	162–167	+72	266	9,060
Methyl palustrate	24–27	+67	265–266	8,530
Levopimaric acid	150–152	−276	272	5,800
Methyl levopimarate	62–64.5	−269	272	5,690
Isopimaric acid	162–164	0	...	...
Methyl isopimarate	61.5–62	0	...	...
Dehydroabietic acid	173–173.5	+62	268 & 276	698 & 774
Methyl dehydroabietate	63–64.5	+61	268 & 276	724 & 740
Abietic acid	172–175	−106	241	24,150
Methyl abietate	...	−96	242	24,300
Neoabietic acid	171–173	+161	252	24,540
Methyl neoabietate	61.5–62	+148	252	24,460

EXPERIMENTAL

An F&M Model 700 gas chromatograph equipped with dual columns and a thermal conductivity detector was used for this study. A 15-foot × 3/16-inch O.D. copper column packed with 5% Versamid 900 on 60 to 80 mesh diatoport S was used to separate the resin acid methyl esters (*3*). The column was operated at 250° C. with helium flow of 150 ml. per minute. The injection port and detector were operated at 300° C. The column was conditioned at the operating temperature overnight and was checked when new and at intervals while in use with a standard mixture of resin acid methyl esters. Stainless steel and aluminum columns were packed and gave the same results as the copper columns. The resin acids were converted to their methyl esters in the injection port by the method of Hetman *et al.* (*4*).

The pine oleoresin or rosin samples were weighed and a known weight of methyl arachidate was added. The sample was titrated to a phenolphthalein end point with 0.10*N* tetramethylammonium hydroxide solution with a microburet. The alkaline solution was evaporated nearly to dryness on a steam bath under a stream of nitrogen and 1 to 2 μl. of the warm oil injected on the gas chromatograph. The peak areas were determined by multiplying the peak height by the width at half height and the per cent sample off the column by comparison of the total resin acid peak area with the peak area of the internal standard. The relative responses of the resin acid methyl esters were calculated by dividing the area of the methyl arachidate peak into the area of the ester peak. All of the resin acid methyl esters except levopimarate have a relative response of 0.78; the methyl levopimarate showed a relative response of 0.56.

Melting points were run in open capillaries and are uncorrected. Optical rotations and ultraviolet spectra were determined in 95% ethanol. All resin acids and methyl esters were essentially pure as indicated by constant physical properties and single peaks off the gas chromatograph.

DISCUSSION

About 2 billion pounds of pine oleoresin and rosin are used each year as raw materials for making paints, varnishes, paper size, and other commercial products. Gas chromatography has been used for the isolation and identification of several resin acids from pine oleoresin and rosin (*7*), and reports on the composition of the acid fraction of several species of pine have been published (*1, 2, 6, 9–14*). The gas chromatographic method for analyzing resin acid mixtures reported by Brooks, Fisher, and Joye (*3*) gave a fast analysis of the resin acids present in pine oleoresin and rosin.

During the past few years the authors have examined the oleoresins and rosins of pines from many parts of the world. These samples included selected and commercial oleoresins and rosins from many pine species. The pine oleoresins were obtained from forest service botanists and the commercial rosins from dealers. This study was originally limited to pine species that have been used or considered for naval stores purposes. In cases where the identity of the oleoresin samples was doubtful or where the composition was unusual, additional samples were obtained from a different source. The gas chromatogram of the resin acids in these samples was characteristic of the species. Some pine species contained different resin acids from others, and all of the species varied in the ratios of acids present. The changes in composition occurring when oleoresin is converted to rosin is shown, and the chemical behavior of some rosins can be correlated with their composition. Some of the rosin samples in Table I were steam distilled in the laboratory and, owing to the milder conditions, may have compositions slightly different than commercial samples of the same rosin.

Besides the analysis of individual species and commercial samples, several hybrids were examined. These hybrids—slash and longleaf, slash and loblolly, and longleaf and loblolly—in most cases produced an oleoresin composition intermediate between the two parents. In a few cases, the male parent contributed more to the composition of the gum than the female parent. There were no instances of the reverse situation.

Samples of tall oil rosin and steam distilled wood rosin listed in Table II contained more abietic and dehydroabietic acids than most gum rosins. Tall oil rosin also contains several early peaks not present in gum rosin. The data in Tables I and II are taken from the oleoresin or rosin that appeared to be typical of the species. Large variations in composition within a species were not observed. The acids were identified by peak retention time relative to an internal standard. In some cases, the peaks may contain minor quantities of unidentified acids.

LITERATURE CITED

(1) Baldwin, D.E., Loeblich, V.M., Lawrence, R.V., *Ind. Eng. Chem.* **3**, 342 (1958).

(2) Bardyshev, I.I., Tkachenko, O.T., Cherches, Kh. A., *Zh. Prikl. Khim.* **38** (9), 2049 (1965).
(3) Brooks, T.W., Fisher, G.S., Joye, N.M., Jr., *Anal. Chem.* **37**, 1063 (1965).
(4) Hetman, N.E., Ault, H.G., Jr., Paylor, R., Feinland, R.J., *J. Am. Chem. Soc.* **42**, 255 (1965).
(5) Hudy, J.A., *Anal. Chem.* **31**, 1754 (1959).
(6) Iconomou, N., Valkanas, G., *Pharm. Acta Helv.* **41**, 59 (1966).
(7) Joye, N.M., Jr., Lawrence, R.V., Gough, L.J., *J. Org. Chem.* **31**, 320 (1966).
(8) Joye, N.M., Jr., Roberts, E.M., Lawrence, R.V., Gough, L.J., Soffer, M.D., Kormon, O., *J. Org. Chem.* **30**, 429 (1965).
(9) Nestler, F.H.M., Zinkel, D.F., *Anal. Chem.* **35**, 1747 (1963).
(10) Norin, T., Westfelt, L., *Acta Chem. Scand.* **17**, 1828 (1963).
(11) Sandermann, W., Weissman, G., *Farbe Lack* **71**, 713 (1965).
(12) Sato, A., Von Rudloff, E., *Can. J. Chem.* **42**, 635 (1964).
(13) Stump, J.H., Jr., Kubitz, K.A., "Naval Stores Review International Yearbook," 14 (1965).
(14) Von Rudloff, E., Sato, A., *Can. J. Chem.* **41**, 2165 (1963).

RECEIVED for review August 22, 1966. Accepted December 30, 1966. The Naval Stores Laboratory is one of the Laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture. Use of a company and/or product name by the department is for the convenience of the reader and does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

Synthesis of Some Halomethylphosphine Oxides

LEON H. CHANCE, DONALD J. DAIGLE, and GEORGE L. DRAKE, Jr.
Southern Regional Research Laboratory, New Orleans, La.

Tris(chloromethyl)phosphine was converted to methyl bis(chloromethyl)phosphine oxide through an oxidation and rearrangement by refluxing in ammonium hydroxide. Tetrakis(bromomethyl)phosphonium bromide was prepared in 93% yield by the reaction of tetrakis(hydroxymethyl)phosphonium chloride and phosphorus pentabromide. The bromide was converted to tris(bromomethyl)phosphine by reaction with aqueous sodium bicarbonate, and the phosphine was converted to tris(bromomethyl)phosphine oxide in 71% yield by oxidizing with aqueous hydrogen peroxide in tetrahydrofuran. Methyl bis(iodomethyl)phosphine oxide was prepared in 47% yield by refluxing methyl bis(chloromethyl)phosphine oxide and sodium iodide in acetone. Infrared and NMR spectra of the subject compounds were recorded.

THE PREPARATION of tetrakis (chloromethyl)phosphonium chloride (I) by the reaction of PCl_5 with tetrakis-(hydroxymethyl)phosphonium chloride (II) was first described by Hoffman (*2*). He also reported the conversion of I to tris(chloromethyl)phosphine (III) by treatment with aqueous $NaHCO_3$ and the oxidation of III to the oxide by boiling with nitric acid. The authors carried out the oxidation with 5% aqueous H_2O_2 in tetrahydrofuran.

Kabachnik and Tsvetkov discovered that the reaction of III with sodium ethylate in ethanol yielded methyl bis(ethoxymethyl)phosphine oxide (*3*). The alcoholysis is accompanied by a redox rearrangement which they termed a "pseudoallyl" rearrangement. They also discovered that the rearrangement of III took place in the presence of hydrochloric acid, and that methyl bis-(chloromethyl)phosphine oxide (IV) was formed. The authors refluxed III with ammonium hydroxide in an effort to form tris(aminomethyl)phosphine. However, a compound was obtained having the identical infrared curve, NMR curve, and melting point of IV. This proved that the rearrangement also takes place in the presence of ammonium hydroxide. Obviously, ammonium hydroxide was not a strong enough base to replace the two remaining chlorine atoms.

Anteunis, Verzele, and Dacremont reported the preparation of tris(bromomethyl)phosphine oxide (V) in only 5% yields from phosphorus pentabromide and diazomethane (*1*). The authors prepared V by a method similar to that used by Hoffman to prepare tris(chloromethyl)phosphine oxide, except that hydrogen peroxide was used instead of nitric acid (*2*). Tetrakis(bromomethyl)phosphonium bromide (VI) (a new compound) was prepared by the reaction of II with PBr_5. Tris(bromomethyl)phosphine, obtained by treating VI with aqueous $NaHCO_3$, was oxidized to V with aqueous H_2O_2 in tetrahydrofuran.

Another compound, methyl bis(iodomethyl)phosphine oxide (VII), was prepared by reacting IV with sodium iodide in acetone.

The same coupling constant, 7 c.p.s., was observed from NMR data for each of the compounds IV, V, and VII. Since each of these compounds contains a different halogen, the authors expected that the coupling constants would be different.

EXPERIMENTAL

Rearrangement and Oxidation of Tris(chloromethyl)phosphine (III) in Ammonium Hydroxide. III (5.95 grams, 0.033 mole) was refluxed with 40 ml. of concentrated ammonium hydroxide for 11 hours. During the reflux, ammonia gas was bubbled into the mixture. The resulting solution was evaporated to dryness, and the solid extracted several times with boiling benzene. After evaporation of the benzene a colorless liquid remained which upon cooling crystallized to a white solid, yield 1.5 grams (28%), m.p. 48–50° C. The infrared spectra (KBr) (Perkin-Elmer Model 137B Infracord) exhibited peaks at 3.28 (w), 3.38 (w), 7.05 (w), 7.1 (w), with a shoulder at 7.2 (w), 7.65 (m), 8.03 (m), 8.3 (s), with a shoulder at 8.15 (m), 8.45 (m), 8.79 (w), 8.88 (w), 10.95 (m) with a shoulder at 10.7 (m), 11.6 (m), 11.9 (w), 13.0 (w), 13.2 (w), 13.7 (w), 13.9 (w), 14.5 (w), and 14.8 μ (w).

The NMR (Varian A-60A Spectrometer) of a deuteriochloroform solution of IV showed a doublet centered at δ 1.7 p.p.m., Jp-ch = 14 c.p.s. and a doublet centered at δ 3.92 p.p.m., Jp-ch = 7 c.p.s. in the ratio of 3 to 4, respectively.

Infrared and NMR spectra were identical with those of methyl bis(chloromethyl)phosphine oxide prepared by the method of Kabachnik and Tsvetkov (*3*).