

Ester	Primary amine	Tertiary amine	Yield, %
Methyl phosphate	Aniline	Dimethylaniline	67.9
Methyl phosphate	$\beta$ -Naphthylamine	Dimethyl- $\beta$ -naphthylamine	64.4
Ethyl phosphate	Aniline	Diethylaniline	99.0
Ethyl phosphate	$\alpha$ -Naphthylamine	Diethyl- $\alpha$ -naphthylamine	60.0
<i>n</i> -Propyl phosphate	Aniline	Di- <i>n</i> -propylaniline	78.1
Butyl phosphate	Aniline	Di- <i>n</i> -butylaniline	78.5

The mixture was treated with 20 ml. of concd. hydrochloric acid dissolved in 30 ml. of water and shaken until the base dissolved. The solution was extracted with two 30-ml. portions of ether and the water layer treated with a 25% sodium hydroxide solution to free the base. The oil which formed was collected by extracting the mixture with ether. The ether was dried over anhydrous sodium sulfate and distilled to recover the tertiary amine.

The yield of isopropylaniline from isopropyl phosphate and aniline was 80.5%.

The boiling points of the amines and the melting points

of their solid derivatives corresponded to those found in the literature.

### Summary

A method has been developed for the preparation of tertiary amines by treating an aromatic amine with alkyl esters of orthophosphoric acid. Six tertiary amines have been prepared in 60 to 99% yield by this procedure.

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## Physical Properties of Terpenes. I. The System $\alpha$ - and $\beta$ -Pinene<sup>1a</sup>

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A knowledge of the physical properties of binary mixtures of  $\alpha$ - and  $\beta$ -pinene is necessary for some phases of study of American gum turpentine which is composed largely of these two substances.<sup>1c</sup>

Data in the literature show a wide variation in the values for the physical constants for  $\alpha$ - and  $\beta$ -pinene. Since it was desired to make a study of binary mixtures of these compounds, it was necessary first to establish constants for the pure substances.

With efficient fractionating columns it is possible to obtain  $\alpha$ - and  $\beta$ -pinenes which, the authors believe, are of a higher degree of purity than has been reported heretofore. In a previous publication<sup>2</sup> the authors have shown that the spiral screen type of column developed by Lecky and Ewell<sup>3</sup> is well suited for the purification of  $\alpha$ - and  $\beta$ -pinene.

### Preparation of $\alpha$ -Pinene and $\beta$ -Pinene

$\alpha$ -Pinene was prepared by the careful fractionation of four liters of commercial  $\alpha$ -pinene,<sup>4</sup> from gum turpentine.

(1a) Original manuscript received April 11, 1942.

(1b) Present address, American Cynamid Co., Stamford, Conn.

(1c) Palkin and co-workers, U. S. D. A. Technical Bulletin No. 276, January, 1932.

(2) Stallcup, Fugitt and Hawkins, *Ind. Eng. Chem., Anal. Ed.*, **14**, 503 (1942).

(3) Lecky and Ewell, *ibid.*, **12**, 544 (1940).

(4) Furnished through the courtesy of Southern Pine Chemical Company, Jacksonville, Florida.

through a spiral screen column<sup>2</sup> at 20-mm. pressure and a reflux ratio of 40 to 1. This column exerted 75 plates upon a mixture of *n*-heptane-methylcyclohexane at total reflux and atmospheric pressure. Fractions were collected at 75-cc. intervals. All fractions with a refractive index in the range 1.4631-1.4633 at 25.0° were combined and refractionated through the same column. Fractions were then collected at 50-cc. intervals and their refractive indices and optical rotations were measured at 25.0°. The fractions which had constant values of refractive index and optical rotation were combined and were considered to be pure  $\alpha$ -pinene. In verification, a 100-cc. portion of the latter was fractionated through a column which had 60 plates determined as above. No change in these two physical constants was noted at any point during collection of the distillate.

For comparison,  $\alpha$ -pinene from wood turpentine was desired. The preparation of this pure component from wood turpentine involved its separation from a small amount of camphene which boils about 3° higher. The intermediate fractions having constant refractive indices and optical rotations at 25.0° were then combined and refractionated. The material thus obtained had constant physical properties and was of the same purity as the  $\alpha$ -pinene from gum turpentine.

The  $\beta$ -pinene used was prepared in an analogous manner from commercial  $\beta$ -pinene<sup>4</sup> obtained from gum turpentine.

These purified pinenes had the following constants

	B. p., °C. (20.0 mm.)	$n_D^{25}$	$d_4^{25}$	$[\alpha]_D^{25}$
$\alpha$ -(gum)	52.2	1.4631	0.8542	- 3.83
$\alpha$ -(wood)	52.2	1.4631	.8542	+34.07
$\beta$ -(gum)	59.7	1.4768	.8666	-21.49

These constants are in close agreement with unpublished

data of J. P. Bain,<sup>5</sup> with much of the data of S. Palkin and co-workers,<sup>1,6</sup> with data of Waterman, Van't Spijker and Van Westen<sup>7</sup> and some of the data of Dupont.<sup>8</sup>

### Experimental

**Density Measurements.**—These were made with a 25-ml. density bottle. In all cases values were obtained at least in duplicate which checked to the fourth decimal place. The thermostat was controlled by means of an Aminco Metastatic Thermoregulator connected to a vacuum tube relay circuit developed by Hershberg and Huntress.<sup>9</sup> The thermoregulator controlled the temperature within a limit of  $\pm 0.02^\circ$ .

Mixtures of  $\alpha$ - and  $\beta$ -pinene were made up to known concentrations by weight. Measurements of the variation of density with concentration were made using  $\alpha$ -pinene from both gum and wood turpentine. The densities of the mixtures were independent of the source of the  $\alpha$ -pinene used. The average deviation of the density determinations was 0.00004. These data may be expressed at  $25.0^\circ$  by the equation

$$d^{25}_4 = 0.8542 + 0.0129X - 0.0005X^2 \quad (1)$$

in which  $X$  is the mole fraction of  $\beta$ -pinene.

**Refractive Index Measurements.**—These were obtained with the pure substances and their mixtures by means of an Abbé refractometer calibrated against a known glass. Constant temperature was maintained by circulating water through the refractometer from the thermostat described above. The average deviation of the determinations was 0.00006.

Refractive index measurements of the two pure substances for the temperature range  $15$ – $35^\circ$  show that both  $\alpha$ - and  $\beta$ -pinene have a coefficient of 0.00045 unit per degree. Observations were made every two degrees, but since the relation is linear only the limiting points are given:  $\alpha$ -pinene,  $n^{15.0}_D$  1.4676,  $n^{35.0}_D$  1.4586;  $\beta$ -pinene,  $n^{15.0}_D$  1.4813,  $n^{35.0}_D$  1.4723.

The variation of the refractive index with concentration for mixtures of  $\beta$ -pinene and either gum or wood  $\alpha$ -pinene at  $25.0^\circ$  may be expressed by the equation

$$n^{25.0}_D = 1.4631 + 0.0144X - 0.0007X^2 \quad (2)$$

where  $X$  is the mole fraction of  $\beta$ -pinene.

The molar refractions of the pure components were calculated using the standard atomic refraction values of Auwers and Eisenlohr and also a value of 0.48 for the cyclobutane ring. In this manner the value of 43.99 was obtained for both  $\alpha$ - and  $\beta$ -pinene. From the observed data the values of 43.93 and 44.40 were calculated for  $\alpha$ -

and  $\beta$ -pinene, respectively, by use of the Lorenz–Lorentz equation. The exaltation of 0.41 for  $\beta$ -pinene is probably due to the presence of the exocyclic double bond. Auwers<sup>10</sup> has proposed that values of from 0.32 to 0.52 be added to correct for the exocyclic double bond.

**Polarimetric Measurements.**—Since  $\alpha$ -pinene has a rotation that varies with its source, sample, and time of year collected from the tree, the value of this constant has no diagnostic significance.<sup>11</sup> It has been pointed out by Dar-mois<sup>12</sup> that  $\beta$ -pinene has a constant specific rotation regardless of its source, and that this value is  $-22.44^\circ$  for the j-line of mercury. Dupont<sup>8</sup> reported a value of  $-22.48^\circ$ .

All rotations were observed at  $25.0^\circ$  in a jacketed two-decimeter tube. A Duboscq polarimeter, reading by vernier to  $0.01^\circ$  of arc and equipped with suitable filters, depending on the wave length of light, was used. Readings on the same tube could be made with an average deviation of  $0.02^\circ$  using the sodium light and  $0.03^\circ$  using a less intense mercury arc.

Listed in Table I are rotations of  $\alpha$ - and  $\beta$ -pinene and their mixtures for the NaD ( $589 \mu\mu$ ), Hg<sub>j</sub> ( $578 \mu\mu$ ) and Hg<sub>v</sub> ( $546 \mu\mu$ ) lines. Also given are the observed rotatory dispersions. Biot's law for the linearity of specific rotations of mixtures does not hold exactly. The maximum deviation is about  $0.3^\circ$  at a mole fraction of 0.5. The data could be expressed by a second degree equation. However, this relation would change with the variation in the value of the rotation of the pure  $\alpha$ -pinene used.

Also, listed in column 3, Table I, are the mole fractions of  $\beta$ -pinene calculated by Biot's law from the observed data using the NaD line. The deviations for the Hg<sub>j</sub> and Hg<sub>v</sub> lines are about the same.

Biot's law may be applied, to express rotatory dispersion for a given mixture, in the form

$$\frac{[\alpha]_v}{[\alpha]_D} = \frac{n_\beta [\alpha_\beta]_v + (1 - n_\beta) [\alpha_\alpha]_v}{n_\beta [\alpha_\beta]_D + (1 - n_\beta) [\alpha_\alpha]_D}$$

in which  $n_\beta$  is the mole fraction of  $\beta$ -pinene in the mixture,  $[\alpha_\beta]_v$  and  $[\alpha_\beta]_D$  are the specific rotations of  $\beta$ -pinene with the v-line and D-line, respectively, and  $[\alpha_\alpha]_v$  and  $[\alpha_\alpha]_D$  are the specific rotations of  $\alpha$ -pinene with the v-line and D-line, respectively. When the values of dispersion are calculated on this basis only slight variations from the observed dispersions are noted. This deviation is illustrated for the  $[\alpha]_v/[\alpha]_D$  dispersion by the data in column 7, Table I.

Dupont<sup>12</sup> observed that for high  $\alpha$ -pinene con-

(5) Private communication.

(6) U. S. D. A. Technical Bulletin No. 596. December, 1937.

(7) Waterman, Van't Spijker and Van Westen, *Rec. trav. chim.*, **48**, 1191 (1929).

(8) Dupont, *Beilstein Suppl.*, Vol. V, pp. 77–79 (1930 ed.).

(9) Hershberg and Huntress, *Ind. Eng. Chem., Anal. Ed.*, **5**, 344–6 (1933).

(10) Auwers, *Ann.*, **387**, 240 (1912).

(11) Black and Thronson, *Ind. Eng. Chem.*, **26**, 66 (1934).

(12) G. Dupont, "Les Essences de Terebenthine," Gauthier Villars and Co., Paris, 1926.

TABLE I  
 SPECIFIC ROTATIONS AND DISPERSIONS OF MIXTURES OF  $\alpha$ - AND  $\beta$ -PINENE

Mole fraction $\beta$ -pinene	$[\alpha]^{25\text{-}0\text{D}}$	Mole fraction $\beta$ -pinene Biot	$[\alpha]^{25\text{-}0\text{J}}$	$[\alpha]^{25\text{-}0\text{V}}$	$[\alpha]_{\text{V}}/[\alpha]_{\text{D}}$	Dev. $\times 10^3$	$[\alpha]_{\text{V}}/[\alpha]_{\text{J}}$
0.000	- 3.83	...	- 4.03	- 4.57	1.193	...	1.134
.110	- 5.69	0.105	- 5.96	- 6.59	1.158	-9	1.106
.205	- 7.32	.198	- 7.61	- 8.29	1.132	-4	1.091
.290	- 8.71	.276	- 9.02	- 9.77	1.121	-4	1.084
.394	-10.53	.379	-10.85	-11.67	1.107	0	1.076
.495	-12.26	.477	-12.61	-13.53	1.103	-2	1.074
.581	-13.84	.567	-14.19	-15.17	1.097	-1	1.070
.680	-15.67	.671	-16.05	-17.13	1.093	-1	1.067
.806	-17.90	.796	-18.32	-19.50	1.089	-1	1.064
.887	-19.44	.884	-19.86	-21.09	1.085	0	1.062
1.000	-21.49	...	-21.98	-23.28	1.083	...	1.059

tent (approximately 70 mole per cent. or greater) the dispersion is a good indication of the  $\alpha$ -pinene content. Ordinarily the  $[\alpha]_{\text{V}}/[\alpha]_{\text{J}}$  ratio is used, probably because the two lines are obtained from the same source. However, the data show that  $[\alpha]_{\text{V}}/[\alpha]_{\text{D}}$  gives a wider dispersion range and therefore should be a more satisfactory indication of  $\alpha$ -pinene content.

**Vapor Pressure Measurements.**—These were determined in the pressure range from 15 to 80 mm. by use of a distillation column in which the vapors were allowed to come to equilibrium with the liquid. The column temperature was adjusted to within  $1.5^\circ$  of the temperature recorded by the condensing vapors in the head. The temperatures of the vapors were measured by the use of a calibrated mercury thermometer that could be read to  $\pm 0.05^\circ$ . The bulb of the thermometer was wrapped with a single layer of cotton gauze.

The pressure was regulated by a manostat of the Hershberg-Huntress type.<sup>9</sup> The action of the vacuum pump on the manostat was partially checked by placing a stopcock between the pump and the manostat. The pressure fluctuations were minimized by including a five-gallon bottle in the system between the manostat and the column.

The manometer was connected to the head of the column so that the pressure of the condensing vapors would be recorded. The vapor pressures were measured with a Germann barometer,<sup>13</sup> using a cathetometer which could be read to 0.01 mm. The observed pressure readings were corrected to  $0^\circ$  for the difference in the expansion of the mercury and the brass scale at different temperatures<sup>14</sup> and were corrected to  $45^\circ$  latitude and sea level.<sup>15</sup> At each recorded temperature about 2 cc. of liquid was collected at a reflux ratio of 20 to 1.

Equations were obtained by applying the method of averages to the corrected data. It was found that the equation

$$\log p = 8.1020 - 2213/T \quad (3)$$

represents the data for  $\alpha$ -pinene for the stated

(13) Germann, *THIS JOURNAL*, **36**, 2456 (1914); built by G. T. Armstrong of this Laboratory.

(14) Lange, "Handbook of Chemistry," Handbook Publishers Co., Sandusky, O., 4th Ed., 1941, p. 1430.

(15) Lange, *ibid.*, pp. 1445-1446.

pressure range. The experimentally determined values agree with the values calculated by the empirical equation with an average deviation of 0.08 mm. and a maximum deviation of 0.2 mm. Similarly, the equation

$$\log p = 8.1504 - 2280/T \quad (4)$$

represents the data of  $\beta$ -pinene for the same pressure range. The experimentally determined values agree with the values calculated by the empirical equation with an average deviation of 0.11 mm. and a maximum deviation of 0.4 mm. From the slopes of the plots the latent heat of vaporization for the stated pressure range may be shown to be 10,130 cal./mole or 74.35 cal./g. for  $\alpha$ -pinene and 10,430 cal./mole or 76.60 cal./g. for  $\beta$ -pinene.

The isobaric vapor-liquid compositions at 20.0 mm. were determined using a modified Sameshima apparatus.<sup>16</sup> About 100 cc. of mixture was placed in the flask and then brought to equilibrium, which was generally attained within two hours but four hours were allowed before a final measurement was made. Samples were then withdrawn from the flask and from the vapor receiver. The rate of flow, which averaged 1.5 cc./min., was regulated by the voltage applied to the internal heater. The thermostat temperature was kept about  $2\text{-}4^\circ$  above the estimated boiling temperature of the liquid. Cold brine solution was circulated through the two condensers, each of which contained a condensing coil made from a four-foot length of glass tubing. Experiments showed that there was no detectable vapor loss four hours after reaching equilibrium between liquid and vapor. The pressure control system was the same one described for the measurements of vapor pressures of the pure compounds. Samples were withdrawn by means of capillary

(16) Sameshima, *THIS JOURNAL*, **40**, 1489 (1918).

TABLE II  
LIQUID-VAPOR COMPOSITION AT 20 MM.

$n_D^{20}$ liquid	Mole fraction $\alpha$ -pinene in liquid	$n_D^{20}$ vapor	Mole fraction $\alpha$ -pinene in vapor
1.4759	0.070	1.4757	0.085
1.4758	.075	1.4756	.090
1.4754	.105	1.4751	.130
1.4751	.130	1.4747	.160
1.4747	.160	1.4742	.195
1.4745	.175	1.4740	.215
1.4731	.280	1.4722	.345
1.4727	.310	1.4718	.375
1.4722	.345	1.4712	.420
1.4718	.375	1.4708	.450
1.4713	.415	1.4702	.495
1.4710	.435	1.4699	.515
1.4706	.465	1.4694	.555
1.4698	.525	1.4686	.610
1.4691	.575	1.4680	.655
1.4689	.590	1.4678	.670
1.4680	.655	1.4671	.720
1.4676	.680	1.4667	.745
1.4668	.740	1.4661	.790
1.4662	.780	1.4656	.825
1.4653	.845	1.4649	.875
1.4650	.865	1.4647	.890
1.4648	.880	1.4645	.905
1.4647	.890	1.4644	.910
1.4641	.930	1.4639	.945
1.4637	.955	1.4636	.965

Table III. Then for each temperature was calculated a liquid mixture composition at 20.0 mm. by applying Raoult's law in the form

$$20.0 = x_{\alpha}p_{\alpha} + (1 - x_{\alpha})p_{\beta}$$

where  $x_{\alpha}$  is the mole fraction of  $\alpha$ -pinene in the liquid phase. The corresponding vapor composition was calculated from the relation

$$y_{\alpha} = \frac{x_{\alpha}p_{\alpha}}{20.0}$$

where  $y_{\alpha}$  is the mole fraction of  $\alpha$ -pinene in the vapor phase. The observed mole fraction of  $\alpha$ -pinene in the vapor, corresponding to liquid composition  $x_{\alpha}$ , in column 4, Table III, was obtained from a plot of the vapor-liquid relations at 20.0 mm., using the data in Table II. The difference between the observed and calculated vapor composition is a measure of the deviation from ideality of the mixtures. These deviations are listed in the last column of Table III.

From the plot of the data in Table II it can be seen that a minimum of 24 theoretical plates at total reflux are required to go from a mixture of 95 mole per cent. to 5 mole per cent.  $\alpha$ -pinene. The same diagram shows a minimum of 50 plates between pure  $\alpha$ - and pure  $\beta$ -pinene under total reflux conditions.

TABLE III  
DEVIATION OF VAPOR CONCENTRATION AS CALCULATED BY RAOULT'S LAW

$t$ , °C.	$p_{\alpha}$ , calcd.	$p_{\beta}$ , calcd.	$x_{\alpha}$ - Mole fraction $\alpha$ -pinene in liquid calcd.	$y_{\alpha}$ - Mole fraction $\alpha$ -pinene in vapor calcd.	$y_{\alpha}$ - Mole fraction $\alpha$ -pinene in vapor obs.	Vapor deviation
52.6	20.39	14.20	0.937	0.955	0.950	0.005
53.0	20.79	14.48	.875	.909	.900	.009
54.0	21.80	15.21	.727	.792	.780	.012
55.0	22.87	15.98	.583	.667	.662	.005
55.5	23.41	16.37	.516	.603	.601	.002
56.0	23.97	16.77	.449	.538	.533	.005
57.0	25.12	17.60	.319	.401	.388	.013
58.0	26.32	18.47	.195	.256	.238	.018
59.0	27.56	19.37	.077	.106	.095	.011
59.4	28.14	19.74	.031	.044	.039	.005

pipets. Data were observed by starting with mixtures rich in  $\alpha$ -pinene and going to mixtures rich in  $\beta$ -pinene and also by starting with mixtures rich in  $\beta$ -pinene and going to mixtures rich in  $\alpha$ -pinene. The compositions were determined by means of refractive index measurements and application of equation (2). The data obtained by this method are recorded in Table II.

In order to compare the observed values with those of an ideal system, pressures,  $p_{\alpha}$  and  $p_{\beta}$ , of the pure components were calculated by equations (3) and (4) for the temperatures listed in

### Summary

The densities, refractive indices and optical rotations for  $\alpha$ - and  $\beta$ -pinene and their mixtures have been determined.

The vapor pressure-temperature relations of  $\alpha$ - and  $\beta$ -pinene were measured in the range of 15 to 80 mm.

The vapor-liquid equilibrium composition data for mixtures of  $\alpha$ - and  $\beta$ -pinene at 20 mm. pressure have been determined.