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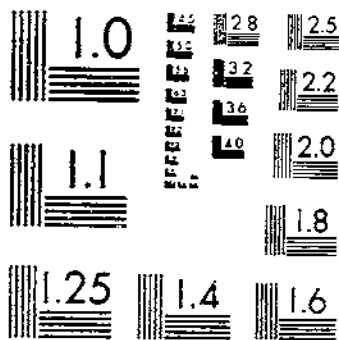
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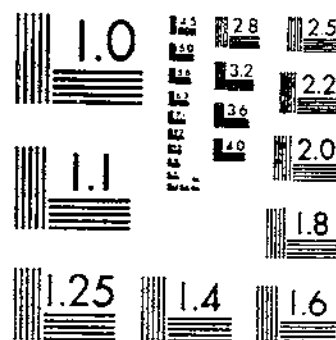
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THE EFFECTS OF VARIOUS METHODS OF BLENDING
COMPOSITION OF AMERICAN GUM TURPENTINE EXCLUSIVE OF THE PINENES
CHADWICK T. CHAPMAN

START



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UNITED STATES
DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

Composition of American Gum Turpentine Exclusive of the Pinenes¹

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INTRODUCTION

For many years turpentine has been almost inseparably associated with paint. Even today, when paint manufacturers are also using other solvents and thinners, the greatest industrial outlet for turpentine is still the paint and varnish industry. However, there is an increasing appreciation of the potentialities of turpentine as a source of organic chemicals and as raw material for the synthesis of chemicals that may find application as plastics, synthetic resins, perfumes, and medicinals.

Commercial turpentine may be roughly divided into two general types, that produced from gum and that produced from wood. Gum turpentine is distilled from the oleoresin of the living tree. In the United States it is obtained principally from two species, longleaf pine and slash pine (*Pinus palustris* Mill. and *P. caribaea* Morel.). A substantial part of the world's gum spirits of turpentine is obtained from other pines in France, Russia, Greece, Spain, Portugal, and to some extent in the Orient. Wood turpentines are produced from wood, that obtained by the steam-solvent process being the most important commercially. Both steam-distilled and destructively distilled wood turpentine are derived from old pine stumps and lightwood. In addition to these sources, the pulping of pine wood by the sulfate process yields turpentine as a by-product.

The production of wood turpentine is mainly in the hands of modern, well-organized chemical industries. The composition and

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properties of these turpentines vary with the different producers and degree of refinement.

In contrast with turpentine of this type, gum turpentine is produced somewhat primitively. The farmer, with his individual still, is the producer of this turpentine. There are some 1,200 gum turpentine stills in the pine belt. In general, in spite of the simplicity of the equipment and the number of independent stills, the quality of the gum turpentine produced is good and fairly uniform. The present trend in the industry, however, appears to be toward central distillation, and a number of central stills have already been placed in operation. The use of central gum stills, with superior equipment and personnel, should lead to even better quality and greater uniformity.

There is a decided difference in the products of the two industries. The wood-turpentine industry manufactures a host of chemical products and is constantly diversifying its products. The gum-turpentine industry, on the other hand, chiefly produces only turpentine as such. Gum turpentine, however, is used to a limited extent by other industries for the manufacture of synthetic products, such as synthetic camphor and terpineol and terpin hydrate.

As a prerequisite for the production and commercial exploitation of its various chemical products, the wood-turpentine industry has found it necessary to make an intensive study of the composition of its raw materials. A great deal of fundamental information on this type of turpentine has thus become available. In contrast with this, the gum-turpentine industry has given little attention to a fundamental study of gum spirits of turpentine. In fact, until a few years ago, beyond the work of Darmois (4, pp. 128-130),³ Dupont and Barraud (5) and Palkin (7), comparatively little was known regarding the composition of even the major terpene constituents, α - and β -pinene. These constitute about 95 percent of the fresh gum spirits. Information on the remaining 5 percent is exceedingly meager, in spite of the fact that it has long been known that this portion exercises an influence, disproportionate to its percentage content, on the yield of synthetic camphor.

A few years ago the major constituents of American gum spirits were reported (7). In a later publication (11) a detailed study of the composition of commercial steam-distilled wood turpentine was reported, and gross differences in the composition of the two kinds of turpentine were pointed out. This comparative study, however, was handicapped by the absence of information on the nonpinene portion of gum spirits. The work reported in this bulletin was undertaken to acquire this much-needed information on the minor constituents of gum spirits, generally referred to as the forerun and tailings, respectively. The low-boiling part, or forerun, although constituting but an insignificant proportion, together with the tailings, may affect the keeping qualities of turpentine.

Dupont (4, pp. 128-130) has examined French turpentine, which resembles American gum spirits of turpentine, and detected dipentene, sobrerol, possibly pinol, a sesquiterpene hydrocarbon distilling around 220° C. at 10 mm., traces of alcohols, and traces of aldehydes or ketones.

While the investigation reported in this bulletin was in progress, Hasselstrom and Hampton reported finding methyl chavicol in gum-

³ Italic numbers in parentheses refer to Literature Cited, page 14.

spirits tailings (6). The presence of methyl chavicol was also known to the writers, and the occurrence of methyl ethers was mentioned in their preliminary report on the subject (15).

One of the writers (8) has reported data showing that even in the ordinary commercial steam distillation of pine oleoresin, fractionation of the pinenes and other constituents takes place to an appreciable extent. In his investigation the increase in the content of β -pinene and tailings in the distillate, although relatively slow during the greater part of the distillation, became more rapid toward the end. However, the extent to which change in distribution would be further accelerated by prolonged distillation, that is, extended beyond the point to which the steam distillation is carried on in commercial practice,⁴ was not determined at that time.

Since β -pinene and the tailings should have considerably greater market value than the original turpentine, the trend in the distillation described above may have commercial importance. In addition, therefore, to information on the composition of the tailings in commercial gum spirits, determination of the yield and composition of the products obtainable by prolonged distillation was deemed desirable.

DISTILLATION EQUIPMENT AND PROCEDURE

The fractionations were carried out in distillation assemblies at suitable pressures, which were maintained constant by a sensitive pressure-control mechanism (9). Operation at accurately reproduced and controlled pressures (2) rendered significant a change of less than 0.1° C. in distillation temperatures, thus permitting a more intelligent cutting of the distillate into appropriate fractions. Temperature changes were read by means of a multiple thermocouple connected through cold junctions to each other and to a potentiometer. Temperature served as a guide in properly timing the introduction of individual fractions into the still pot for systematic refractionation.

Most of the fractionations were carried out in gauze-plate columns, the one shown in figure 1 being a typical assembly. The columns were surrounded with hot-air jackets similar to the one described by Bruun (1). In the later part of the distillation work, particularly in the fractionation of high-boiling liquids at low pressures, a wound glass-fiber antibumping and boiling-promoting device (10) was used. Some of the final refractionations of the forerun were carried out in a semi-micro packed column (11).

The initial fractionations were run in batches. As the elimination of the pinenes progressed, it was possible to combine concentrates of the minor constituents. These composites were then systematically refractionated.

HEADS OR FORERUN

The turpentine (sample A) used for the investigation of the heads or forerun represented the first 10 percent of the steam distillate of a commercial charge of longleaf pine oleoresin. Dissolved water was removed as ice by chilling to -20° C. The turpentine thus dehydrated had the following properties: Sp. gr., $\frac{15.5}{15.5}$, 0.8663; n_D^{20} , 1.4698;

⁴ In commercial practice it is customary to discontinue the steam distillation and draw off the rosin when the turpentine-water ratio of the distillate is somewhat less than 1:10 and the temperature of the rosin is about 157° C.

α_D^{20} , $+16.8$; Engler distillation, initial 153°C ., 98 percent distilled below 165°C .

The turpentine was then subjected to systematic fractional distillation under reduced pressure. The more highly volatile material that passed the water condenser was collected in a solid carbon dioxide trap. Only compartment *a* of the trap (fig. 1) was packed with solid carbon dioxide. The heads from 31 kg. of turpentine were thus con-

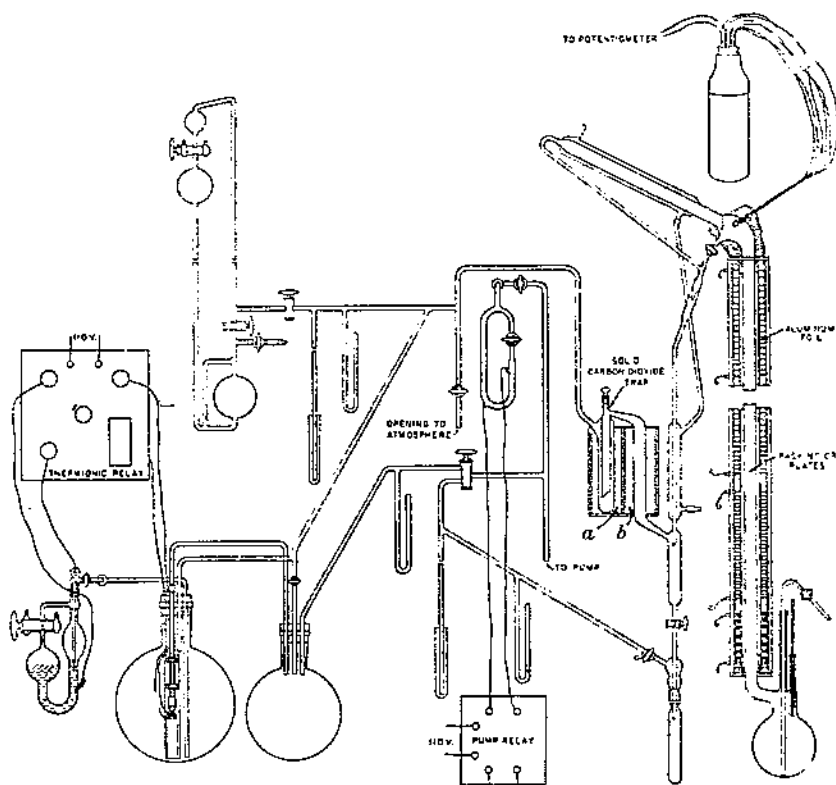


FIGURE 1.—Fractionating assembly.

centrated into three fractions. These concentrates, which still contained large proportions of α -pinene, had the properties shown in table 1.

TABLE 1.—Properties of fractions that distilled below the distillation temperature of α -pinene

Fraction	Weight	Boiling range	Pressure	Observed optical rotation ¹ (α_D^{20})
	<i>Grams</i>	<i>° C.</i>	<i>Mm.</i>	<i>Degrees</i>
1.....	19	53-70	51	+15.5
2.....	78	62-63.5	34	+27.5
3.....	76	63.5-63.7	34	+29.5

¹ Pure α -pinene from sample A had a rotation of $+31.0^\circ$.

² Throughout this bulletin this symbol indicates observed optical rotation read in a decimeter tube.

After four systematic refractionations, a new series of fractions was obtained. The properties of the first five fractions of this series are shown in table 2.

TABLE 2.—Properties of refractionated material that distilled below the distillation temperature of α -pinene

Fraction	Weight	Boiling range at 700 mm.	Refractive index (n_D^{20})	Density (d_4^{20})	Observed optical rotation (α_D^{20})
	Grams	°C.			Degrees
1.....	3½	56-63	1.3776	0.800
2.....	4	63-102	1.4105	
3.....	4	102-120	1.4400	
4.....	4	120-145	1.4485	
5.....	12	145-156	1.4630		+24.6

The first four fractions, totaling approximately 15 cc., represent the greater part of the heads, or portion boiling below the distillation temperature of α -pinene. Each fraction boiled over a wide range of temperature, indicating that no pure compounds were separated in any of these fractions. The fifth fraction was about 80-percent α -pinene. The results of this distillation indicate that the total forerun or material boiling below α -pinene constitutes at most 0.07 percent of the original turpentine. This is taken as the maximum, since the sample was obtained from the first 10 percent of a charge and should have been somewhat richer in forerun than the commercial turpentine as a whole. Further investigation of this part is awaiting collection of larger samples.

TAILINGS

The turpentine (sample B) used in the investigation of the tailings was a portion of the last 10 percent⁶ distilled from a commercial distillation of longleaf oleoresin.

The turpentine had the following constants: Sp. gr., $\frac{15.5}{15.5}$, 0.8747; n_D^{20} , 1.4739; α_D^{20} , +3.9; Engler distillation, 89 percent distilled below 170° C.

In order to remove the rosin carried over during the commercial distillation, the turpentine was redistilled with steam. The residue was then subjected to vacuum distillation, and the portion that did not distill below 100° C. at 1 mm. was considered nonvolatile. Examination of this semisolid nonvolatile residue, which amounted to 0.4 percent of the original turpentine, showed that it had a high percentage of resin acids.

Twenty-six kilograms of this redistilled turpentine was subjected to repeated fractional distillation in order to eliminate the pinenes⁷ and to concentrate the tailings. After several refractionations, a series of 50 fractions, boiling above β -pinene and totaling 2 kg., was obtained. The physical properties of these fractions are shown in

⁶ This portion was collected because it has been found (7) that the last 15 percent of a normal commercial distillation of gum spirits contains a higher proportion of β -pinene and tailings than does commercial gum spirits. The Darms (7) method of calculation indicated that this sample contained about 45 percent of α -pinene, about 47 of β -pinene, and 7.7 of tailings.

⁷ A previous investigation (7) has shown that, except for the small amount of forerun, the fractions distilling below the tailings contain only α - and β -pinene.

table 3 and in figure 2. A number of compounds were obtained in high concentrations in various fractions, as indicated in table 3 and shown by breaks in the curves in figure 2.

TABLE 3.—Physical and chemical properties of tailings fractions

Fraction No.	Distillation temperature	Pressure	Refractive index (n_D^{20})	Observed optical rotation (α_D^{20})	Density (d_4^{20})	Hydroxyl ¹	Methoxyl ²	Ratio of fraction to total tailings	Sum of fraction	Ratio of fraction to turpentine
	$^{\circ}$ C.	Mm.		Degrees		Percent	Percent	Percent	Percent	Percent
1.	59.7-60.0			-18.2				3.6	3.6	0.28
2.	60.0-61.0		1.4760	-16.20	0.8617			2.1	5.7	.16
3.	61.0-64.0		1.4743	-13.12	.8480			1.6	7.3	.12
4.	64.0-69.0		1.4732	-8.20	.8283			1.6	8.9	.12
5.	69.0-70.5		1.4743	-5.41	.8352			1.0	9.9	.05
6.	70.5-71.0		1.4751	-3.18	.8309			1.4	11.3	.11
7.	71.0-71.3		1.4753	-1.60	.8405			1.7	13.0	.11
8.	71.3-71.5		1.4752	-1.05	.8413			2.0	15.0	.13
9.	71.5-71.7		1.4754	-.30	.8413			1.8	16.8	.14
10.	71.7-71.7+		1.4759	+1.15	.8412	0.05	0.2	11.1	27.9	.85
11.	71.7-72.0		1.4756	+1.51	.8411			1.5	29.4	.12
12.	72.0-73.0		1.4756	+1.32	.8408			2.4	31.8	.18
13.	73.0-76.0		1.4771	+1.51	.8421	.2		1.8	33.6	.14
14.	76.0-85.0	20	1.4629	-2.80	.8813	1.4	.2	3.5	37.1	.27
15.	85.0-93.0		1.4791	-7.98	.9313	2.6		1.4	39.5	.11
16.	93.0-97.0		1.4784	-4.82	.9444			1.3	39.8	.10
17.	97.0-98.6		1.4834	+2.80	.9484	6.0	2.8	1.3	41.1	.10
18.	98.6-99.7		1.4981	+7.00	.9525			1.3	42.4	.10
19.	99.7-100.6		1.4909	+9.00	.9557			1.4	43.8	.11
20.	100.6-101.1		1.4939	+12.05	.9616	6.2	4.3	1.4	45.2	.11
21.	101.1-101.3		1.4953	+13.91	.9622			1.4	46.6	.11
22.	101.3-101.6		1.4969	+15.40	.9630			1.4	48.0	.11
23.	101.6-102.0		1.4981	+16.38	.9652	5.8	7.0	1.4	49.4	.11
24.	102.0-102.2		1.4993	+17.18	.9655		7.4	1.2	50.6	.09
25.	102.2-102.4		1.5004	+17.80	.9662		7.9	1.4	52.0	.11
26.	102.4-102.6		1.5013	+18.07	.9667	5.5	8.5	1.4	53.4	.11
27.	102.6-103.3		1.5025	+16.20	.9648		9.8	5.0	58.4	.38
28.	99.0-89.5		1.5086	+15.59	.9650		10.6	3.0	61.4	.23
29.	89.5-90.0		1.5051	+13.07	.9649	3.7	11.8	3.0	64.4	.23
30.	90.0-80.5		1.5059	+10.80	.9640		12.3	2.4	66.8	.18
31.	90.5-91.0		1.5076	+5.30	.9644	2.8	13.4	2.6	69.4	.20
32.	91.0-91.5		1.5071	+2.85	.9647	2.8	11.2	1.4	70.8	.11
33.	91.5-92.0		1.5068	-.43	.9647		10.7	1.9	72.7	.15
34.	92.0-92.5		1.5031	-3.86	.9652			1.8	74.5	.14
35.	92.5-95.0	10	1.4941	-6.95	.9657			2.0	76.5	.15
36.	95.0-97.0		1.4925	-10.28	.9691	3.6	3.5	1.7	78.2	.13
37.	97.0-98.0		1.4764	-12.50	.9705			1.0	80.2	.15
38.	98.0-98.4		1.4753	-12.90	.9715	4.8		1.6	81.8	.12
39.	98.4-98.7		1.4751	-12.70	.9725	4.6	.4	1.6	83.4	.12
40.	98.7-99.0		1.4751	-12.35	.9718			2.2	85.6	.17
41.	99.0-99.5		1.4775	-11.53	.9713	5.3		1.6	87.2	.12
42.	99.5-100.0		1.4793	-11.00	.9708			1.3	88.5	.10
43.	87-91	5	1.4821	-8.73	.9682			1.2	89.7	.09
44.			1.4900	-1.00	.9670	8.1	.5	2.0	91.7	.15
45.	103-104.2	10	1.4887	+1.82	.9609	7.2	.3	1.5	93.2	.12
46.	104.2-106.5		1.4891	+7.40	.9534	7.5	.3	1.4	94.6	.11
47.	94-101	5	1.4871	+4.10	.9472	6.8	1.3	1.5	96.1	.12
48.	101-107		1.4943	-5.45	.9682	5.7	7.6	1.1	97.2	.08
49.			1.5105	-5.31	1.004	3.1	20.5	1.7	98.9	.13
50.			1.4965	+1.88	.9879	6.2	1.9	1.1	100.0	.08
Total								100.0		7.68

¹ Theoretical hydroxyl equivalent of $C_{10}H_{17}OH$ equals 11.03 percent.

² Theoretical methoxyl equivalent of $C_{10}H_{17}OC_2H_5$ equals 20.05 percent.

Fractions 45 to 50 were not included in the final refractionation because of their high boiling points. Fraction 44 is the residue from the final refractionation of the tailings. Fraction 50 is the residue from the first series of fractions.

³ The distillation temperature ranged from 107° at 5 mm. to 103° at 3 mm.

Progress in the separation of the hydrocarbons from the alcohols and methyl ethers was followed also by the determination of hydroxyl by the Zerevitinoff method (12, p. 156; 16), and of methoxyl by the Viebeck and Schwappach method as modified by Clark (5).

DISCUSSION OF DATA IN FIGURE 2

The sharp angles in both the density and the refractive index curves between 5 and 10 percent indicate that here there was a concentration of some compound, the properties of which pointed to *p*-menthane, the saturated cyclic hydrocarbon previously identified in steam-distilled wood turpentine. Because of the small quantity available and the presence of substantial proportions of β -pinene, it was not possible to obtain this compound in pure form by further fractionation. However, a portion of fraction 4 (table 3) was dissolved completely in mild fuming sulfuric acid, indicating the absence of a stable saturated hydrocarbon. The most probable unsaturated compound appears to be *p*-menthene. An attempt was made to

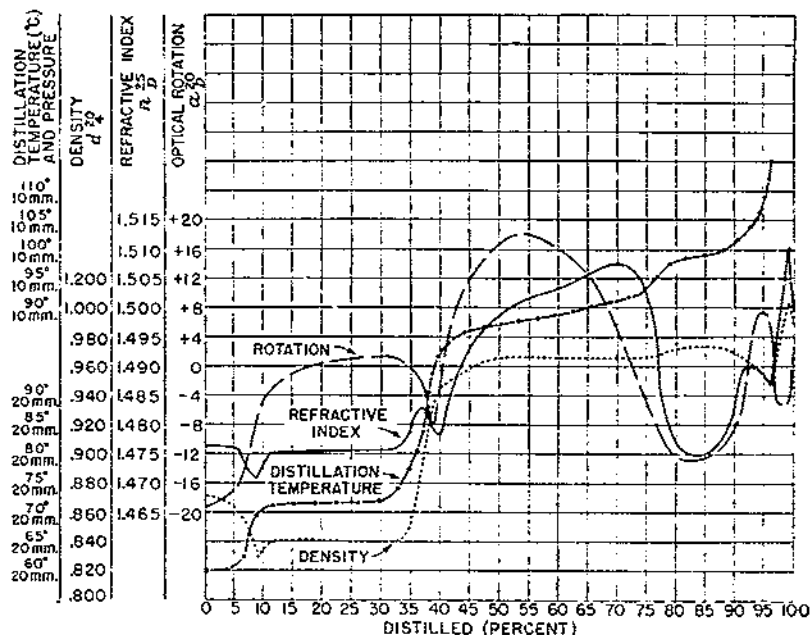


FIGURE 2.—Physical properties of fractions of tailings (table 3).

prepare a nitrosyl chloride, but none could be isolated, probably because of the admixture of β -pinene and dipentene.

Horizontal portions of all the curves between 10 and 35 percent are due to the separation of dipentene. The slight slope of the rotation curve (fig. 2) is attributed to the presence of a small amount of active limonene. The dipentene was identified as the tetrabromide.

A maximum appears on the refractive index curve and a minimum on the optical rotation curve in the region of 37 percent. Hydroxyl determinations indicate that the fractions in this region contain approximately 20 percent terpene alcohols (see table 3). These changes may be due to the appearance of the terpene alcohol.

The minimum in the refractive index curve at 40 percent and the flattening of the density curve near this point are due to terpinolene, identification of which is described later.

About 35 percent of the tailings was a mixture of methyl chavicol

and terpene alcohols distilling over a range of 10° C. The density curve in this region (42 to 77 percent) is nearly flat, indicating a pure compound (fig. 2). This is only apparent, however, and is due to the fact that methyl chavicol and terpene alcohols have approximately the same densities. The refractive index curve reaches a maximum at 70 percent, and methoxyl determinations (see table 3) show that methyl chavicol reaches a maximum of 64 percent at this point. The rotation curve reaches a maximum at 54 percent. This is in agreement with the hydroxyl determinations, which show that terpene alcohol reaches a maximum of about 50 percent at this point. The maximum in the rotation curve at this point is presumably due to concentration of alcohols.

Between 80 and 87 percent the distillation curve flattens out, the density curve reaches a maximum, and the refractive index a minimum. These results are due to the concentration of inactive bornyl acetate,⁸ identification of which will be described later.

Hydroxyl determination (table 3) shows that the quantity of terpene alcohol is at a minimum near 72 percent, the point at which the rotation curve crosses the zero rotation line. After reaching a minimum, the quantity of terpene alcohols again increases as the negative rotation increases.

The percentage of hydroxyl continues to increase, while the rotation curve passes through a minimum and reaches a maximum at 95 percent. Near this point, the refractive index and the density curves reach a minimum.

The refractive index and the density curves reach a maximum near 99 percent, and the rotation curve (fig. 2) reaches a minimum near this point. The percentage of methoxyl also reaches a maximum at this point. These results are probably due to another alkyl ether of some type. The minimum in the rotation curve may be due to a change from one alcohol to another. The percentage of hydroxyl reaches a minimum value at this point.

All the higher boiling fractions were tested for phenols with diazo-*p*-nitrobenzene (11). Fractions 46 to 50, inclusive, table 3, gave positive tests, indicating that at least part of the hydroxy compounds in those fractions were phenolic.

CHEMICAL SEPARATION OF THE ALCOHOLS IN THE MATERIAL DISTILLING BELOW 100° C. AT 10 MM.

Since hydroxyl determinations showed that the first 34 percent of the tailings contained only a little terpene alcohol, the chemical separation of the alcohols was confined to the portion between 34 and 89 percent. The 30 fractions involved were recombined into 5 portions, and each portion was treated with butyl borate to separate the alcohols.

After active hydrogen was determined by the Zerevitinoff method, 1 mole of butyl borate was added for each 2 moles of hydroxyl. The mixture was placed in the distillation flask, of a vacuum distillation assembly, held at a pressure of 50 mm., and heated in an oil bath at 80° C. for 15 minutes. The temperature of the oil bath was then gradually increased to 125°, and at the same time the pressure was lowered to approximately 1 mm. The reaction mixture was held at this temperature and pressure for 15 minutes after distillation had practically stopped. The vacuum distillate contained butyl alcohol, the excess

⁸ Greek turpentine (4, p. 116) contains about 1 percent of inactive bornyl acetate.

butyl borate, and compounds without hydroxyl groups. The alcohols, having been converted to nonvolatile borates, remained in the distillation flask.

The alcohols, recovered from the borates by steam distillation, were found to be a complex mixture. The borate residues remaining after the steam distillation of the alcohols were diluted with petroleum ether. A solid separated from the residues from portions 2 and 3. Its properties, which are described later, correspond to those given in the literature (13, 14) for inactive pinocarveol hydrate.

Fenchyl alcohol, if present, should have been found in portions 1 and 2. None, however, was detected by the methods used to identify it in steam-distilled wood turpentine (11).

The alcohols from portions 1 to 5 were kept at -20° C. for several weeks. Those from portion 3 yielded a small quantity of low-melting crystalline material. Data obtained on this material (p. 11) indicated that it might be inactive pinocarveol.⁹

EXAMINATION OF THE NONALCOHOLS DISTILLING ABOVE DIPENTENE AND BELOW 100° C. AT 10 MM.

The vacuum distillate (containing the nonalcohols) was thoroughly washed with water to remove butyl alcohol. The five portions, freed of alcohols, total 700 gm. Their properties are shown in table 4.

TABLE 4.—Properties of nonalcohols

Portion	Density d_{4}^{20}	Refractive index n_{D}^{25}	Methoxyl	Temperatures at which bulk distilled at 10 mm.
			Percent	$^{\circ}$ C.
1	0.8956	1.4800	2.3	68-90
2	.9544	1.4836	85-100
3	.9582	1.5052	16.1	88-100
4	.9670	1.5064	15.6	91-100
5	.9732	1.4712	95-105

These portions were subjected to systematic fractional distillation and a series of fractions was obtained having the properties indicated in table 5 and figure 3.

TABLE 5.—Refractionation of nonalcohols¹ listed in table 4

Fraction No.	Distillation temperature at 10 mm.	Refractive index (n_{D}^{25})	Density (d_{4}^{20})	Methoxyl	Ratio of fraction to whole		Ratio of fraction to total tailings		Ratio of fraction to tur- pentine
					Percent	Percent	Percent	Percent	
	$^{\circ}$ C.				Percent	Percent	Percent	Percent	
1	51-65.5	1.4777	0.86	3.0	3.0	1.1	0.08	
2	65.5-67.0	1.4825	.8692	0.25	2.5	5.5	0.07
3	67.0-68.0	1.4828	.8801	.52	2.2	7.7	0.06
4	68.0-90.59195	0.4	17.1
5	80.5-87.5	1.4854	.9392	14.0	32.0	0.25
6	87.5-90.0	1.5026	.9495	0.7	41.7	0.40
7	90.0-91.0	1.5086	.9608	16.0	11.5	53.2	0.26
8	91.0-91.3	1.5134	.9640	18.7	21.5	74.7	0.32
9	91.3-91.8	1.5080	.9655	6.7	81.4	0.58
10	91.8-94.0	1.4886	3.2	84.6	0.18
11	94.0-95.0	1.4801	2.8	87.4	0.08
12 ¹	95.0-96.0	1.4624	.9754	2.3	5.8	93.2	0.15
13 ¹	1.4636	.9820	2.4	6.8	100.0	0.19
Total	100.0	35.1	2.60

¹ Represents 35 percent of the tailings.

² Approximate.

³ This fraction had a saponification number of 232, equivalent to 81 percent of bornyl acetate.

⁴ Residue. This fraction had a saponification number of 260, equivalent to 91 percent of bornyl acetate.

⁵ Pinocarveol (dextro) has been reported by Schmidt (15) as one of the auto-oxidation products of β -pinene.

TERPINOLENE

The distillation temperature curve and the refractive index curve show breaks from 5 to 8 percent, indicating a high concentration of a compound in this region. The compound was identified as terpinolene by its tetrabromide.

BORNYL ACETATE

The distillation temperature and the density curves in figure 3 indicate that a compound was concentrated between 87 and 100 percent in the distillation. The sharp break in the refractive index curve at this point indicates that a compound with a much lower refractive index than that of methyl chavicol was distilling just above the distillation temperature of that compound. Inactive bornyl acetate was identified in fraction 13, table 5.

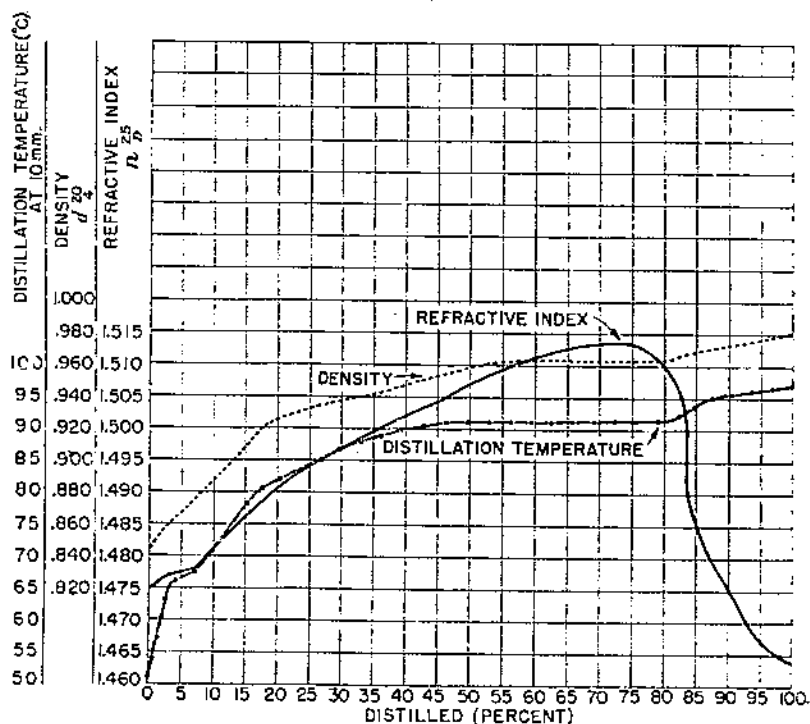


FIGURE 3.—Physical properties of fractions of alcohol-free tailings that distilled between 65° and 100° C. at 10 mm. (table 5).

METHYL CHAVICOL

The distillation-temperature curve flattens out between 45 and 80 percent (fig. 3), indicating that a considerable quantity of pure compound separated. The refractive index curve, however, merely reaches a maximum, indicating that the product is not entirely pure. Methoxyl determinations also indicate that the purity of methyl chavicol, the principal constituent in this region, ranges from 75 to 89 percent, and then back to 75 percent again.

Fractions 6, 7, and 8, table 5, representing 43 percent of the material in table 5, were systematically refractionated. Forty percent distilled from 91° to 91.2° C. at 10 mm. Methoxyl determination indicated that it was 91 percent pure methyl chavicol. Saponification indicated that this cut (91° to 91.2°) also contained 9 percent of bornyl acetate, which had not been completely removed by fractionation because its distillation temperature was so near that of methyl chavicol.

This cut had the following constants: d_4^{20} , 0.9665; n_D^{25} , 1.5167. It did not solidify when held at -20° C. for several weeks.

SOLID ISOLATED FROM BORATE RESIDUES

The solid isolated from the borate residues was recrystallized several times from benzene. Table 6 shows the properties of the purified crystals. Those listed by Schmidt (13, 14) for pinocarveol hydrate are given for comparison.

TABLE 6.—*Properties of solid from borate residues and of pinocarveol as reported by Schmidt*

Material	Melting point	Molecular weight ¹	Results of combustion		Specific optical rotation ([α] _D)
			C	H	
Recrystallized solid.....	° C. 182-183	334	Percent 70.3	Percent 10.80	Degrees +4
Active pinocarveol hydrate (13, 14).....	190-191	338	70.48	10.74	±31
Inactive pinocarveol hydrate (13, 14).....	176-177				0
Calculated for $(C_{15}H_{15}O)_2$		340	70.53	10.67	

¹ By the camphor method.

² Corrected.

ALCOHOL SEPARATED BY COOLING TO -20° C.

About half a gram of the alcohol was shaken with dilute sulfuric acid. A small quantity of solid, m. p. 178°-179° C., which was not present in the starting material, was obtained. When it was mixed with the solid isolated from the borate residue, there was no depression of the melting point. The phenyl urethane also was prepared. Table 7 shows the properties of the alcohol. Those listed by Schmidt for pinocarveol are given for comparison.

TABLE 7.—*Properties of alcohol separated at -20° C. and of pinocarveol as reported by Schmidt*

Material	Melting point	Phenylurethane		Melting point of hydrate
		Melting point	Nitrogen content	
Low-melting crystals.....	° C. Below 0	° C. 89-100	Percent 4.95	° C. 178-179
Active pinocarveol (13, 14).....	+7	89-90		190-191
Inactive pinocarveol (13, 14).....		95-96		176-177
Calculated for $C_{17}H_{17}O_2N$			5.16	

¹ Corrected.

PREPARATION OF DERIVATIVES OF ISOLATED COMPOUNDS

DIPENTENE

Four grams of fraction 10, table 3, was dissolved in a mixture of amyl alcohol and ether, cooled to 0° C., and brominated by the dropwise addition of 9 gm. of bromine. The crystals isolated from the reaction mixture were recrystallized from absolute ethyl alcohol. The tetrabromide melted at 124°–125°, and when it was mixed with authentic dipentene tetrabromide it caused no depression of the melting point.

TERPINOLENE

The tetrabromide of fraction 2, table 5, was prepared by the same procedure used to prepare dipentene tetrabromide. The bromide melted at 118°–119° C., and when it was mixed with authentic terpinolene tetrabromide there was no depression of the melting point.

INACTIVE BORNYL ACETATE

For identification purposes, 3 gm. of fraction 13, table 5, was saponified with alcoholic sodium hydroxide. On dilution with water, borneol separated and was filtered off. After drying somewhat, the crude product was sublimed to eliminate tarry material, and it was then recrystallized from petroleum ether. The crystals had an optical rotation of -2° ($[\alpha]_D$), melted at 207°–208° C., and when mixed with authentic borneol showed no depression of the melting point.

The alkaline solution was extracted with ether to remove tarry material, then was acidified with sulfuric acid until acid to Congo paper, and distilled. The distillate was made alkaline to phenolphthalein with sodium hydroxide and evaporated. The *p*-toluidide, prepared in the usual way, melted at 148°–149° C. No depression of the melting point resulted when the *p*-toluidide was mixed with authentic acetyl *p*-toluidide.

METHYL CHAVICOL

Five grams of the methyl chavicol that distilled between 91.0° and 91.2° C. at 10 mm. was oxidized at room temperature by shaking with 300 cc. of 4-percent potassium permanganate. The manganese dioxide was filtered off, and the filtrate was concentrated to 100 cc. and acidified with hydrochloric acid. The precipitated anisic acid was recrystallized from water and melted at 185°–186°. When mixed with authentic anisic acid, there was no depression of the melting point.

After removal of the anisic acid by filtration, ether extraction of the concentrate yielded about a gram of crude homoanisic acid. After recrystallization from water, the acid melted at 86° to 87°.

PROLONGED STEAM DISTILLATION OF PINE OLEORESIN

In order to determine the extent to which the rise in concentration of β -pinene and tailings and the corresponding decrease in α -pinene observed in commercial steam distillation of the oleoresin (β) may

be accelerated by prolonged or extended distillation, the period of distillation of a commercial charge (about 8 barrels) of slash pine oleoresin was extended 2 hours beyond the normal turning out point. The oily distillate was collected in two parts.

Part 1, consisting of about 2½ gallons of oily distillate, was collected during the first 45 minutes of the 2-hour period. It had the following properties: Sp. gr., $\frac{15.5}{15.5}$, 0.8782; n_D^{20} , 1.4709; α_D^{20} , -16.72; acid number, 3; methoxyl, 1.2 percent.

Part 2, consisting of slightly more than a quart of oily distillate, was collected during the last 75 minutes of the 2-hour period. It had the following properties: Sp. gr., $\frac{15.5}{15.5}$, 0.9077; n_D^{20} , 1.4909; α_D^{20} , -11.52; acid number, 13; methoxyl, 3.2 percent.

Both parts 1 and 2 were fractionally distilled in vacuum. The physical properties, saponification numbers, and methoxyl and hydroxyl values of the fractions were determined, and the composition of each part was calculated from these data. In table 8 the results are compared with those obtained on the turpentine (sample B) used in the main investigation.

TABLE 8.—Calculated compositions of parts 1 and 2 of the distillate from the prolonged commercial steam distillation of turpentine and of sample B

Constituents	Part 1 †	Part 2 †	Sample B ‡ of turpentine
	Percent	Percent	Percent
α -pinene.....	23	10	45
β -pinene.....	43	28	47
Dipentene.....	15	14	2
Other hydrocarbons.....	4	6	1
Methyl chavicol.....	5	13	1.3
Alcohols, esters, and other alkyl ethers.....	2	5	2
Resin and other nonvolatile matter.....	5	16	.4

† From slash pine oleoresin.

‡ Sample B represented the last 10 percent of turpentine distilled from a commercial distillation of longleaf oleoresin. It contained a higher proportion of β -pinene and tailings than normal gum turpentine.

SUMMARY AND CONCLUSIONS

Gum turpentine derived from longleaf pine (*Pinus palustris*) was fractionally distilled, and the materials distilling below α -pinene and above β -pinene were separated. The samples of turpentine used in this investigation were the first (richer in forerun) and last (richer in tailings) portions, respectively, of commercial distillations of gum. They were found to contain 0.07 percent of forerun and 7.7 percent of tailings.

About 2 kg. of tailings was subjected to repeated fractional distillation. It was found to have the following gross composition: About two-fifths was monocyclic hydrocarbons, about one-fifth was terpene alcohols and phenols, and about two-fifths was a mixture consisting principally of ethers and esters.

The chemical and physical data of the final series of fractions, when correlated and considered in the order of ascending distillation temperatures, showed the constituents in the tailings to be approximately as follows: (1) A small quantity of an unsaturated hydrocarbon having properties similar to *p*-menthene; (2) considerable dipentene

(about one-fourth), which appeared to contain a little *d*-limonene; (3) a small quantity of terpinolene; (4) a considerable proportion (about one-third) consisting essentially of a mixture (approximately equal quantities) of methyl chavicol and alcohols; (5) a portion (about one-sixth) that was essentially bornyl acetate but also contained alcohols and a small quantity of alkyl ether; (6) hydroxy compounds that were in part phenolic, another alkyl ether, and esters other than bornyl acetate.

The alcohols appeared to be a complex mixture. Fenchyl alcohol, one of the predominant alcohols in the tailings of steam-distilled wood turpentine, could not be detected. A solid having the properties of pinocarveol hydrate was isolated, and also an alcohol that was solid at low temperature and had properties similar to pinocarveol.

A study was made of the component distribution trend in commercial turpentine-still operation. The increase in β -pinene over α -pinene and the increase in tailings constituents were decidedly accelerated in the fractions obtained by prolonged distillation. Such constituents as dipentene, alcohols, and methyl chavicol (easily isomerized to anethol) increased to such an extent that, for example, the oil collected during a 45-minute period of prolonged distillation had a concentration of dipentene about seven times as great as that in the turpentine examined (sample B) and a concentration of methyl chavicol about four times as great.

No attempt was made to determine the commercial feasibility of obtaining additional β -pinene and tailings constituents by prolonged distillation.

A description of fractionating assemblies adapted to vacuum fractionation is given.

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