

TABLE VI.—FRACTIONAL DISTILLATION OF THE VOLATILE OIL FROM *Pinus radiata*

Fraction	Distillation Range		Distillate, %	Density, d_4^{25}	Index of Refraction, n_D^{25}	Specific Rotation, $[\alpha]_D^{25}$
	Pressure, Mm.	Temperature, ° C.				
1	740	100-154	1
2	740	154-155	27	0.8578	1.4690	-1.73°
3	740	155-157	22	0.8587	1.4693	-3.84°
4	740	157-158	11	0.8601	1.4718	-7.57°
5	740	158-159	7	0.8628	1.4743	-11.90°
6	740	159-160	6	0.8659	1.4734	-13.40°
7	740	160-161	2	0.8666	1.4746	-14.47°
8	740	161-162	5	0.8638	1.4746
9	740	162-163	15	0.8660	1.4748	-13°
10	740	163-169	2
Residue	2

TABLE VII.—FRACTIONAL DISTILLATION OF THE VOLATILE OIL FROM *Pinus Virginiana*

Fraction	Distillation Range		Distillate, %	Density, d_4^{25}	Index of Refraction, n_D^{25}	Specific Rotation, $[\alpha]_D^{25}$
	Pressure, Mm.	Temperature, ° C.				
1	740	153-154	41	0.8552	1.4680	-2.36°
2	740	154-155	17	0.8543	1.4703	-5.50°
3	740	155-156	40	0.8546	1.4704	-4.66°
4	Residue	2

turpentine contained approximately 75 per cent *dl*- α -pinene and 22 per cent *l*- β -pinene.

Pinus virginiana oleoresin consisted of 77 per cent of rosin and 23 per cent of turpentine. The turpentine consists almost entirely of α -pinene (90 per cent of *dl*- α -pinene and 8 per cent of *l*- α -pinene).

Thus composition of turpentines of the five pine species studied is very simple, consisting in four cases chiefly, if not completely, of α - and β -pinenes and in one case of α -pinene alone.

Chemical composition of turpentine of *Pinus cembra* (*sibirica*) from Russia, as reported by Shkateloff, and that of *P. cembra* (a geographically separate tree) from Austria, as found by us, is

apparently very similar. On the other hand, composition of *P. strobus* turpentine was found to be different from the morphologically closely related but geographically separated *P. monticola*. While these two species are difficult to distinguish by external characters, their turpentines are different inasmuch as *P. monticola* (from California) contains *n*-undecane and *P. strobus* does not. Analysis of *P. monticola* turpentine from Idaho is in progress.

REFERENCES

- (1) Mirov, N. T., *Ann. Rev. Biochem.*, **17**, 521 (1948).
- (2) Lombard, R., *Compt. Rend.*, **222**, 237 (1946).
- (3) *Moniteur Scientifique*, Ser. 4, **22**, part 1, 217-227 (1908).
- (4) Hepting, G. H., *Science*, **105**, 209 (1947).

Composition of Gum Turpentine of *Pinus lambertiana**

By N. T. MIROV, A. J. HAAGEN-SMIT, and JAMES THURLOW

The composition of gum turpentine obtained from *Pinus lambertiana* has been determined and the results of the study are reported.

SUGAR PINE, or *Pinus lambertiana*, is the most majestic of all pines, reaching a height of 225

feet and a diameter of 10 feet. It grows from southern Oregon to lower California. In California, where it is best developed, it is found in mixture with other conifers at middle elevations of mountain ridges. Botanically it belongs to the subgenus *Haploxylon* or the white pines.

STUDIES

In 1913, turpentine of sugar pine growing at an elevation of 5800 feet was obtained by steam distilla-

* Received April 4, 1949, as a joint contribution from the California Forest and Range Experiment Station, maintained by the Forest Service, U. S. Department of Agriculture, in cooperation with the University of California, Berkeley, and the Kerckhoff Laboratories of the Biological Sciences, California Institute of Technology, Pasadena.

tion and analyzed by Schorger (1) with the following results:

Turpentine in oleoresin.....	16.4%
Density, d_{4}^{20} , of turpentine.....	0.8663
Index of refraction, n_D^{20}	1.4728
Specific rotation, $[\alpha]_D^{20}$	+10.42°

The composition of turpentine was reported as follows:

<i>d</i> - α -pinene.....	70-75%
β -pinene.....	about 5%
Probably phellandrene.....	2-3%
Probably aliphatic hydrocarbon...	2-3%
A sesquiterpene of an aromodendrene type	

Oleoresin for the present work was obtained by the members of the Institute of Forest Genetics in 1947 in the Sierra Nevada Mountains, at an elevation of about 3500 feet. Twenty trees yielded, in two months, about 10,000 Gm. of honey-like oleoresin that remained liquid after prolonged storage. In some samples rosin acids precipitated reluctantly; in others they did not precipitate at all. Turpentine was obtained by distilling the oleoresin under reduced pressure. Toward the end of the distillation, the temperature inside the flask was 200° and the pressure was 0.02 mm.

The turpentine was distilled at atmospheric pressure until the temperature reached 187° and the distillation was then continued at 38 mm. until the temperature reached 183°. Finally the pressure was reduced to 0.1 mm. and the distillation was discontinued when the temperature reached 250°. The distillation characteristics of the turpentine and the physical constants of the fractions are listed in Table I.

Several high-boiling fractions were analyzed for carbon and hydrogen. The results of this analysis are listed in Table II.

The fractionation data show an accumulation of material at 154-162° and at 166-175° at atmospheric pressure. The presence of α -pinene in the interval 154-156° was shown by the preparation of *dl*- α -pinene nitrosochloride, having a melting point of 112°. No melting point depression was observed when the nitrosochloride was mixed with an authentic pinene nitrosochloride. The oxidation of fraction 164-166° gave nopinic acid, melting point 125°. From the fractionation data and the physical constants of the fraction we may conclude that the distillate contains approximately 65% *l*- α -pinene and 13% *l*- β -pinene.

Judging from its physical constants, fraction 11, boiling point 175-180°, contained a monocyclic

TABLE I.—FRACTIONAL DISTILLATION OF THE VOLATILE OIL FROM *Pinus lambertiana*

Fraction No.	Distillation Range		Distillate, %		Density, d_{4}^{20}	Index of Refraction, n_D^{20}	Specific Rotation, $[\alpha]_D^{20}$
	Pressure, Mm.	Temperature, °C.	Observed	Cumulative			
1	742	148-152	0.4	1.4581
2	742	152-154	4.6	5.0	0.8536	1.4656	-15.52°
3	742	154-156	29.6	34.6	0.8536	1.4667	-16.56°
4	742	156-158	14.0	48.6	0.8541	1.4691	-17.75°
5	742	158-160	9.4	58.0	0.8554	1.4713	-19.12°
6	742	160-162	5.6	63.6	0.8554	1.4734	-19.24°
7	742	162-164	3.7	67.3	0.8565	1.4743	-19.62°
8	742	164-166	1.4	68.7	0.8577	1.4749	-18.72°
9	742	166-170	3.7	72.4	0.8577	1.4749	-17.30°
10	742	170-175	3.6	76.0	0.8577	1.4750	-16.37°
11	742	175-180	1.6	77.6	0.8536	1.4738	-12.12°
12	38	88-103	0.4	78.0	0.8774	1.4808	+ 0.43°
13	38	103-123	0.6	78.6	0.8995	1.4884	+12.94°
14	38	123-133	2.7	81.3	0.9169	1.4970	+27.84°
15	38	133-141	7.4	88.7	0.9187	1.4983	+32.49°
16	38	141-143	3.0	91.7	0.9187	1.4993	+33.30°
17	38	143-148	3.3	95.0	0.9169	1.4997	+31.36°
18	38	148-158	1.2	96.2	0.9164	1.5005	+25.30°
19	38	158-163	0.6	96.8
20	38	163-183	0.7	97.5
21	0.1	130-137	1.1	98.6	0.8937	1.4993	+ 7.35°
22	0.1	137-144	0.6	99.2	0.8995	1.5015	+ 4.38°
23	0.1	144-248	0.4	99.6	1.5165
Residue	0.4	100.0

A measure of 5690 Gm. of oleoresin yielded 1045 Gm. of turpentine (or 18.4%), having the following characteristics:

Density, d_{4}^{20}	0.8669
Index of refraction, n_D^{20}	1.4753
Specific rotation, $[\alpha]_D^{20}$	-7.46°

Schorger's turpentine was dextrorotatory. In the present tests, 15 turpentine samples, obtained from individual trees, were analyzed. The specific rotation $[\alpha]$ varied from -18.25° to -1.35°. That is, all 15 samples were levorotatory.

TABLE II.—CARBON-HYDROGEN ANALYSES OF DISTILLATION FRACTIONS OF *Pinus lambertiana* TURPENTINE

Fraction	Temperature Range, °C.	C, %	H, %	Total
14	123-133 at 38 mm.	86.16	11.59	97.75
15	133-141 at 38 mm.	87.24	11.96	99.20
16	141-143 at 38 mm.	87.63	11.70	99.03
17	143-148 at 38 mm.	87.84	11.81	99.65
20	163-183° at 38 mm.	83.39	11.54	94.93
21	130-137 at 0.1 mm.	87.70	11.95	99.65
22	137-144 at 0.1 mm.	87.66	11.97	99.63

a Semisolid.

terpene with two double bonds. This fraction did not yield any crystalline derivative with the methods used for the identification of dipentene, terpinene, and carene.

Fraction 12, boiling point 83–88° at 38 mm. or 181–187° at 740 mm., contains a mixture of hydrocarbon- and oxygen-containing derivatives. Terpineol, borneol, as well as other alcohols, were absent as shown by the Tschugaeff and Zerewitinoff (2) method. Saponifications showed the presence of only traces of ester. It is probable that this fraction contains some isomerization and oxidation products of pinene.

Fractions 15–18, boiling between 133 and 158° at 38 mm., contain hydrocarbon as seen from Table II. Attempts at preparing various halogen derivatives from these fractions were unsuccessful. Dehydrogenations were carried out on these fractions according to the method of Melville (3). The absence of any blue color in the dehydrogenated material showed the absence of azulenic sesquiterpenes. A phosphoric acid-petroleum ether partition confirmed this. Picrates were prepared from both the phosphoric acid portion and the petroleum ether portion. The melting points were found to be 114–115°, as compared to Melville's value of 115–116° for cadalene picrate.

The molecular refraction found for fractions 14, 15, 16, 17, and 18 are, respectively, 65.19, 65.24, 65.34, 65.50, and 65.61. For a sesquiterpene with 2 double bonds and 2 rings the molecular refraction, M_D , would be 66.1. These fractions contain, therefore, bicyclic sesquiterpenes of cadalene type structure.

Fraction 20, b. p. 163–183° at 38 mm., contained white crystals which could be separated from the oil on a porous plate. After recrystallization from ethyl alcohol, the crystals melted at 133°. Analysis showed that the crystals were composed of 80.67% of

carbon and 11.94% of hydrogen. Calculated for a sesquiterpene alcohol $C_{15}H_{26}O$, the composition would be: carbon 81.08%; hydrogen 11.71%. Molecular weight of the crystalline substance was: found 213; calculated molecular weight for $C_{15}H_{26}O$, 229. Since this alcohol differs from all known sesquiterpene alcohols, the name Lambertol is introduced for this compound.

The fractions distilling at 0.1 mm. from 130–144° consist of hydrocarbons, probably diterpenes.

Saturated hydrocarbons were not present as shown by a treatment of the oil with fuming sulfuric acid.

SUMMARY

The volatile oil of *Pinus lambertiana* contains 65 per cent *l*- α -pinene, 13 per cent *l*- β -pinene, 10 per cent bicyclic sesquiterpene of cadalene type, 2 per cent sesquiterpene alcohol, $C_{15}H_{26}O$, m. p. 133° (Lambertol), and 2 per cent unidentified polyterpenes. It is seen that the results of the present investigation are at variance with the results obtained by Schorger. Although presence of α - and β -pinenes was verified, phellandrene and an aliphatic hydrocarbon were not detected. On the other hand, the sesquiterpene fraction was more fully explored.

REFERENCES

- (1) Schorger, A. W., "An Examination of the Oleoresins of Some Western Pines," *Forest Service Bulletin* 119, 1913, Washington, D. C.
- (2) Soltys, Arnulf, *Mikrochemis*, 20, 107 (1936).
- (3) Melville, J., *J. Am. Chem. Soc.*, 55, 2462 (1933).

The Decomposition of Sodium Phenobarbital in Solutions of Aliphatic Amines and Alkanolamines*

By MELVIN F. W. DUNKER

The decomposition of aqueous solutions of sodium phenobarbital proceeds at room temperature in the presence of aliphatic amines and alkanolamines to produce the previously reported phenylethylacetylurea. The mixtures had pH values ranging between 10.2 and 10.6, whereas the aqueous solution of sodium phenobarbital had a pH of 9.2. In some cases crystals of the ureide formed within fifteen minutes after mixing the liquids.

IN CONNECTION with the reaction product of theophylline and phenobarbital, first noted with an aqueous solution containing aminophylline and sodium phenobarbital (1), it was

called to the author's attention (2) that an aqueous solution of sodium phenobarbital containing ethylene diamine within a few days deposited white crystals melting at 147–148°. The instability of aqueous solutions of soluble phenobarbital and other barbiturates has been reported in several papers summarized by Husa and Jatul (3) On the basis of the melting point, mixed melting point with the ureide prepared directly from ethylphenylacetic acid, and analytical data, it was evident that the white crystalline solid was ethylphenylacetylurea previously reported as one of the decomposition products of sodium phenobarbital.

* Received Dec. 15, 1948, from the College of Pharmacy, Wayne University, Detroit, Mich.