

Composition of Gum Turpentine of Pines*

XVIII. A Report on *Pinus pungens*, *P. glabra*, and *P. teocote*

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Pinus pungens Lamb. (table-mountain pine) is a tree which in a forest occasionally reaches 60 feet in height, with a trunk two to three feet in diameter; when open-grown, it is rather scrubby—20 to 30 feet high, with a short, thick trunk. Its cones are two to three and one-half inches long, roundish, and armed with hooked, curved spines. *Pinus pungens* grows on dry gravelly slopes and ridges of the Appalachian Mountains from southern Pennsylvania to North Carolina, eastern and middle Tennessee, and Georgia. A sample of oleoresin was collected from trees of this species in Buncombe County, N. C., at an elevation of 2,400 feet. Unfortunately, some of the liquid part of the sample was lost in transit, and the yield of turpentine was rather low—only 14.5%. The turpentine was separated from the oleoresin *in vacuo*, so that at the end of the distillation the temperature was 170° and pressure was 1 mm. The turpentine possessed the following characteristics: d_4^{23} , 0.8564; n_D^{23} , 1.4682; $[\alpha]_D$, -23.7.

A batch of 200 Gm. of the turpentine was distilled in a 90-cm. Todd column equipped with a heated jacket and a stillhead permitting a 10:1 reflux ratio. Results of the distillation are shown in Table I.

Fraction 2 was tested for presence of α -pinene. Pinene nitroschloride¹ recrystallized three times from chloroform by means of methanol had a melting point of 106.5°.

Fractions 10 and 11 combined were tested for presence of β -pinene¹ by oxidizing the oil with 24 Gm. of potassium permanganate and 5 Gm. of sodium hydroxide in 600 cc. of water. Water was then evaporated in an open beaker to 200 cc. Abundant precipitate of sodium nopinate was formed upon cooling the solution. Nopinic acid was prepared by dissolving sodium nopinate in dilute sulfuric acid and was extracted by shaking the solution with ether. After three recrystallizations from benzene, nopinic acid melted at 126–127°.

Limonene was identified in Fraction 17 by preparing a tetrabromide¹ possessing a melting point of 117–118°. The pot residue (6.5 Gm.) boiling above 176° was redistilled in a 10-cc. flask. More than 3 Gm. distilled at 175–176°; the remaining oil became dark and apparently partly polymerized.

Judging by the distillation behavior, *Pinus pungens* gum turpentine consisted of about 70% *l*- α -pinene; 20% *l*- β -pinene and 8–9% *l*-limonene. The polymerized residue amounted only to about 1% of the weight of the oil.

Pinus glabra Walt. is the spruce pine of the southeastern United States. In South Carolina it is called king's tree; in Florida, poor pine, which shows the inconsistency of common names. Spruce pine attains its largest size—up to 120 feet in height—in northwestern Florida. It grows as far west as southeastern Louisiana.

A sample of oleoresin was obtained by John K. Gross, U. S. Forest Service, from five trees growing in the DeSoto National Forest, Perry County, Miss. Oleoresin, 3,500 Gm., was distilled under reduced pressure. Toward the end of the distillation, the temperature of the oleoresin was 150°; the pressure was 0.05 mm. The yield of turpentine was 22.3%.

The turpentine possessed these characteristics: d_4^{23} , 0.8599; n_D^{23} , 1.4735; $[\alpha]_D$, -4.65°.

A batch of 500 Gm. was subjected to fractional distillation in a Todd column 90 cm. long and 25 mm. inside diameter. The reflux ratio was 10:1. The results are given in Table I.

Fraction 2 was examined for α -pinene. Pinene nitroschloride melted at 107°; β -pinene was identified in fraction 10 by preparing nopinic acid, which, after three recrystallizations from benzene, melted at 125°.

Fraction 18 (6 cc.) was brominated in 1:1 ether-ethanol mixture. An abundant precipitate was formed when 3.5 cc. of bromine was added. The melting point of the tetrabromide after several recrystallizations from ethyl acetate was 106°.

Fraction 21 was tested for a sesquiterpene. Dry HCl gas was bubbled through a solution of the oil in absolute ether. Crystals were formed after the treated solution was kept under refrigeration for two weeks. These crystals, however, melted at room temperature. By suction filtration while cold, some white crystals, which melted at 48–49°, were isolated.

Pinus teocote Schlecht et Cham. is a widely distributed, variable Mexican pine, growing at elevations ranging from 4,500 to 10,000 feet. It occurs from the Northern States of Durango, Coahuilla, and Nuevo Leon to Guatemala. It has a casual resemblance to *Pinus leiophylla* and the natives often call both by the same name, "pino chino." Sometimes it is called "pino rosillo." A sample of oleoresin of this pine was collected under the supervision of Forest Engineer, Cenobio E. Blanco—an expert on Mexican pines—at El Salto, Durango, at an elevation a little over 8,000 feet.

A batch of 914 Gm. of the oleoresin was distilled at reduced pressure, so that at the end of distillation, the temperature in the flask reached 203° and the pressure was 0.8 mm. The yield of turpentine was 24.2%.

The crude turpentine had the following physical characteristics: d_4^{23} , 0.8578; n_D^{23} , 1.4669; $[\alpha]_D^{23}$, +7.6°.

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¹ For methods used see previous articles of this series in THIS JOURNAL.

TABLE I.—FRACTIONAL DISTILLATION OF TURPENTINES OF *PINUS PUNGENS*, *P. GLABRA*, AND *P. TECOTE*

Fractions	Boiling Range, ° C.	Distillate, %	Density, d_{4}^{25}	Index of Refraction n_D^{25}	Optical Rotation $[\alpha]_D^{25}$, Degrees
<i>Pinus pungens</i> (200 Gm. Used)					
1	150-155	0.9	...	1.4630	-10.0
2	155-156	42.8	0.8549	1.4663	-10.0
3	156-157	17.5	...	1.4672	-10.7
4	157-158	3.0	...	1.4700	-11.2
5	158-159	4.7	...	1.4700	-12.0
6	159-160	2.4	...	1.4715	-13.7
7	160-161	0.9	...	1.4727	-13.7
8	161-162	1.4	...	1.4740	-16.0
9	162-163	2.0	...	1.4753	-17.0
10	163-164	4.0	0.8614	1.4770	-18.0
11	164-165	3.2	0.8612	1.4770	-20.0
12	165-166.5	3.2	...	1.4773	-24.2
13	166.5-168	2.1	...	1.4770	-30.0
14	168-169	2.0	...	1.4789	-36.0
15	169-171	2.2	...	1.4767	-44.0
16	171-173	1.3	...	1.4759	-54.3
17	173-176	3.0	0.8423	1.4750	-70.5
Residue and losses	...	3.4
<i>Pinus glabra</i> (500 Gm. Used)					
1	155-157	1.4	0.8556	1.4678	+16.5
2	157-158	20.5	0.8563	1.4683	+16.5
3	158-159	10.5	0.8577	1.4694	+12.5
4	159-160	6.4	0.8586	1.4710	+ 8.3
5	160-161	5.1	0.8584	1.4720	+ 4.4
6	161-162	5.4	0.8584	1.4732	+ 0.7
7	162-163	3.6	0.8584	1.4743	- 3.3
8	163-164	6.1	0.8607	1.4754	- 7.4
9	164-165	11.9	0.8617	1.4772	-13.3
10	165-166	14.3	0.8617	1.4784	-19.0
11	166-167	4.2	0.8614	1.4785	-23.3
12	167-168	2.0	0.8593	1.4782	-28.4
13	168-169	1.3	0.8580	1.4779	-34.0
14	169-171	1.1	0.8548	1.4770	-40.7
15	171-173	0.6	0.8506	1.4767	-50.0
16	173-175	1.6	0.8447	1.4759	-62.7
Continuation of distillation at 10 mm. pressure:					
17	60-62	0.4	0.8433	1.4755	-67.7
18	62-63	1.2	0.8443	1.4764	-66.3
19	63-65	0.6	0.8497	1.4776	...
20	65-75	0.1	0.8574	1.4801	-60.0
21	75-90	0.2	0.8623	1.4949	-25.0
22	90-95	0.1	...	1.5000	...
23	95-125	0.1	...	1.5007	...
Residue and losses	...	1.3
<i>Pinus teocote</i> (203 Gm. Used)					
1	151-154.8	3.7	0.855	1.4657	+ 7.5
2	154.8-156	82.6	0.855	1.4661	+ 7.6
3	156-157	1.6	0.855	1.4673	+ 5.8
4	157-161	2.5	0.854	1.4711	+ 0.8
Continuation of distillation at 8 mm. pressure. Fraction 8 at 1 mm.:					
5	58-76	1.6	0.855	1.4783	+ 2.0
6	76-86	0.4	0.872	1.4805	+ 4.0
7	86-90	1.2	0.905	1.4890	+ 8.2
8	80	1.5	0.930	1.5007	+30.6
Residue and losses	...	4.9

A batch of 203 Gm. of the turpentine was fractionated in a 90-cm. 12-mm. inside diameter Todd column packed with glass helices. A reflux ratio of 12:1 was maintained. After a distillate equal to 90.4% of the charge had been received at atmospheric pressure, the residue in the pot (13.1 Gm.) was distilled at reduced pressure through a 3-in. Vigreux column at reduced pressure, using a 4:1 re-

flux ratio. The results of the fractionation are shown in Table I.

The first two fractions had constants close to those of α -pinene. During the collection of fraction 2 there was almost no variation in physical properties and the majority of the fraction boiled over a 0.2° range. α -Pinene was identified in fraction 2 by preparation of *dl*- α -pinene nitroschloride, which

melted at 103–104° after two recrystallizations from chloroform by addition of cold methanol. A mixed melting point determination with authentic *dl*- α -pinene nitrosochloride showed no melting point depression. A nitropiperidide, m. p. 120°, was also prepared.

Fraction 8 had the properties of a sesquiterpene. From 1.4 Gm. of fraction 8, 0.4 Gm. of crude sesquiterpene hydrochloride was prepared. The sesquiterpene hydrochloride melted at 58–59° after two recrystallizations from glacial acetic acid. There was no depression in melting point upon ad-

mixture with a sample of hydrochloride from *d*-longifolene derived from *P. ponderosa* from the Black Hills, South Dakota.

To sum up, *Pinus pungens* turpentine consisted of *dl*- and *l*- α -pinene, 70%; *l*- β -pinene 20%; *l*-limonene 8–9%. *Pinus glabra* turpentine contained *dl*- and *d*- α -pinene, 45%; *l*- β -pinene, 45%; *l*-limonene, 8%; and possibly a small amount of sesquiterpene containing hydrochloride with very low melting point. *P. teocote* from Durango, Mexico, yielded turpentine consisting of 92% *dl*- and *d*- α -pinene, and 3% of sesquiterpene, the major constituent of which is *d*-longifolene.

Nitroalkyl Ethyl Carbonates*

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A laboratory method has been developed for the preparation of nitroalkyl ethyl carbonates. Four new mixed carbonates were synthesized in which the nitroalkyl group varied from butyl to heptyl.

THE PROPERTIES of aromatic nitro compounds have been known for many years. However, our knowledge of aliphatic nitro derivatives is considerably less. The physiological activity of certain nitro alkyl sulfonates has been reported (1). Because of the activity shown by this structure, it seemed worth-while to prepare a series of nitro alkyl carbonates for pharmacological testing. The information obtained from this testing would be a contribution to our knowledge of the relationship between chemical structure and pharmacological action.

A survey of the literature revealed that alkyl carbonates had been known since 1873 when Lieben (2) reported the preparation of di-*n*-butyl carbonate. Chattaway (3) extended the study of carbonates by reacting phosgene with aliphatic alcohols. No mention was found in the literature pertaining to nitroalkyl carbonates. It is the

purpose of this paper to report our method of preparing mixed nitroalkyl carbonates by the reaction of ethyl chloroformate and nitroalkyl alcohols together in the presence of a suitable catalyst.

EXPERIMENTAL

Procedure.—The procedure developed for the preparation of the carbonates listed in Table I is outlined in detail. One-half mole of ethyl chloroformate and 0.5 mole of the nitroalcohol were placed in a 1-L. three-neck flask fitted with a mechanical stirrer, dropping funnel, and a thermometer. Twenty-two grams (0.55 mole) of sodium hydroxide previously dissolved in 200 ml. of distilled water and cooled to room temperature was added dropwise to the rapidly stirred mixture while the reaction temperature was maintained at 20–25° by external cooling. Agitation was continued for an hour after addition of the aqueous alkali. Sufficient distilled water was added to the flask to dissolve the sodium chloride, the mixture transferred to a separatory funnel, and the salt solution drawn off. The water-immiscible liquid was washed free of chlorides and dried over anhydrous sodium sulfate. Vacuum distillation yielded unreacted starting material, the desired product, and a high boiling residue. The mixed carbonates were light yellow in color, had a fruity odor, did not react with α -naphthyl isocyanate, and gave a positive qualitative test for a nitro group. Table I gives the physical and chemical constants of the mixed ethyl carbonates prepared from 2-nitrobutanol-1,¹ 2-nitro-2-methylpropanol-1,¹ 4-nitro-2-methylhexanol-3, and 3-nitroheptanol-4. The latter two nitroalcohols were prepared by the method of Vanderbilt (4).

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