

Composition of Gum Turpentine of Pines. XXIV*

A Report on Two Asiatic Pines: *Pinus armandi* and *P. bungeana*

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Composition of the total oil of *P. armandi*, both light (82% of the total) and heavy (18%) is approximately as follows: *l*- and *dl*- α -pinene, 44%; *l*-camphene, 2%; *l*- β -pinene, 4%; *l*-limonene, 17–18%; *n*-undecane, 1%; *l*-bornyl acetate, 6.5%; a bicyclic sesquiterpene, b_{12} , 116–118°, 3.5%; a bicyclic sesquiterpene related to cadalene, 9%; "albicaulol," 1.5%; cembrene, 4.5%; a diterpene which gave a maleic anhydride adduct, 1%; pot residue and loss, 6%. *P. bungeana* turpentine is of a very simple composition: 60–65% *d*- and *dl*- α -pinene; 30–35% *l*- β -pinene and about 2 or 3% of unidentified higher-boiling fractions, presumably sesquiterpenes. Composition of turpentine of *P. bungeana*, thus, differs very much from that of *P. armandi*. It also differs from *P. Gerardiana* in almost complete absence of sesquiterpenes, and in its β -pinene being levorotatory.

Pinus armandi Franchet grows wild in the mountains of western China, where it is widely distributed and usually found in rocky places, rarely forming pure forests. It was originally discovered by Pere David in 1873, south of the Yellow River in Shensi, and subsequently by other travelers in Yunnan, Hupeh, and Szechuan, and more recently in Formosa. Shaw (5) put it together with *Pinus flexilis* in the group *Flexiles*.

A gallon sample of oleoresin, accompanied with foliage and cones, was received in 1953 from the Mutual Security Agency, Taipei, Formosa.¹ The oleoresin was collected at an elevation of 1,200–1,600 meters above sea level from a scattered stand of trees sixty to eighty years of age. The oleoresin was very liquid and light in color.

A batch of 2,510 Gm. was subjected to heating under reduced pressure. Eight hundred grams of turpentine distilled at a temperature of 150–170° and at a pressure of about 10 mm. Hg. This part of the distillate was designated as light oil. Then the temperature was increased to 210° and the pressure was reduced to 2 mm. Hg and additional 175 Gm. of distillate was obtained. The oil was viscous and yellow. It was designated as heavy oil. As a whole, the products obtained by processing the oleoresin were as follows: Oil—light, 800 Gm. or 32 per cent; oil—heavy, 175 Gm. or 7 per cent; water, 70 Gm. or 2.8 per cent; impurities, 10 Gm. or 0.4 per cent. The oil in the water-free pure oleoresin amounted to 40.1 per cent.

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The physical properties of the gum turpentine from *P. armandi* were as follows: Light oil: d_4^{24} , 0.8635; n_D^{23} , 1.4701; $[\alpha]_D^{24}$, -31.3. Heavy oil: High density and refractive index. Owing to the formation of crystals of a sesquiterpene alcohol in the oil, on standing at 0°, the exact properties were not taken.

THE LIGHT OIL OF *P. ARMANDI*

A batch of 745 Gm. of the light oil was distilled through a 25-mm. inside diameter, 90-cm. long, Todd column packed with $3/32$ -inch single turn glass helices, maintaining a reflux ratio of 10:1 and a pressure of 12 mm. of Hg. The results of the distillation are shown in Table III.

The physical properties of Fractions 1 and 2 were close to those for pure α -pinene. A good yield of *dl*- α -pinene nitrosochloride was prepared from Fraction 1. After several recrystallizations, the melting point was 103–104°, and the melting point was not depressed by admixture of authentic *dl*- α -pinene nitrosochloride. A nitrolpiperidide was prepared from the nitrosochloride. The nitrolpiperidide melted at 119–120° and was not depressed in melting point by admixture with an authentic sample of *dl*- α -pinene nitrolpiperidide.

The maximum in optical rotation and density in Fractions 3 and 4 indicated the possible presence of camphene. A part of Fractions 3 and 4 was hydrated by the method of Bertram and Walbaum (1). The ester received was hydrolyzed giving a poor yield of an alcohol, isolated by steam distillation, and recrystallized from petroleum ether (b. p. 30–60°) several times until it melted at 211–212°. No melting point depression was noted on admixture with a purified commercial sample of *dl*-isoborneol.

Fraction 5 was a transition fraction containing β -pinene and camphene.

Fraction 6 was redistilled through a 6-inch Vigreux column. A heart cut had the following properties: b_{760} , 163–166°; d_4^{23} , 0.851; n_D^{23} , 1.4738; $[\alpha]_D^{23}$, -20.3. A 5-Gm. portion of the heart cut was oxidized with alkaline permanganate by the method of Wallach (7). The sodium nopinate (0.36 Gm.) was converted to nopinic acid which, after recrystallization from water, melted at 125–

126°. It showed no melting point depression on admixture with authentic nopinic acid.

Fraction 7 is mostly *l*- β -pinene. Fractions 8, 9, 10, and 11 are mainly *l*-limonene. A portion of fraction 10 was redistilled in a Claisen flask over sodium at atmospheric pressure. A heart cut with the following characteristics was obtained: b_{760} , 175.5–176.5°; d_4^{25} , 0.838; n_D^{25} , 1.4728; $[\alpha]_D^{25}$, –116. A tetrabromide was received, which, when recrystallized from ethyl acetate at 0°, melted at 103–104° and on admixture with authentic limonene tetrabromide showed no depression in melting point.

Fraction 12 was a small transition fraction. The properties of Fractions 13 and 14 indicated the presence of a saturated hydrocarbon. The oil of these fractions was shaken with concentrated sulfuric acid followed by several portions of fuming sulfuric acid. The oil was washed with water, dried with sodium sulfate, and distilled over sodium. The properties of the oil received (2.6 Gm.) are compared with those of *n*-undecane in Table I.

TABLE I.—PROPERTIES OF A SATURATED HYDROCARBON FROM FRACTIONS 13 AND 14

	<i>n</i> -Undecane from <i>P. armandi</i>	<i>n</i> -Undecane ^a
n_D	1.4166 ^{22,8}	1.41902 ²⁰
d_4	0.7362 ²³	0.7404 ²⁰
b_{760}	196–197	195.8

^a Egloff, G., "Physical Constants of Hydrocarbons," Vol. 1 Am. Chem. Soc. Monograph No. 78, Reinhold Publishing Corporation, New York, 1939, p. 76.

Fraction 15 was a transition fraction and Fractions 16, 17, and 18, were *l*-bornyl acetate. Fraction 17 crystallized solid on standing in the refrigerator. About 12 Gm. of crystalline bornyl acetate was removed from the fraction by repeated crystallization at 0°. Some of the bornyl acetate was recrystallized from petroleum ether (b. p. 30–60°) and had the following properties: m. p. 27–28°; $[\alpha]_D^{25}$, –44.8; c = 5.02 in 95% ethanol. One Gm. of Fraction 17 was saponified by refluxing in alcoholic potassium hydroxide. After making the saponification solution acid, borneol precipitated out. The borneol melted at 207–208° after recrystallization from petroleum ether (b. p. 30–60°) and yielded a 3,5-dinitrobenzoate m. p. 139–140°. Fractions 16 and 18 both crystallized to a solid mass, yielding bornyl acetate, m. p. 27° when seeded and kept at 0°. Fraction 19 was a transition fraction and yielded some bornyl acetate by seeding.

Fractions 20 to 26 contained sesquiterpenes. There are evidently two sesquiterpenes in the oil. One is most concentrated in Fraction 21 and the other in Fraction 26.

Fraction 21 has a molecular refraction R_D = 65.6 and gave a color test for aromadendrene (2). A 0.26-Gm. yield of crude hydrochloride was received from 3 ml. of Fraction 21. After two recrystallizations the hydrochloride melted at 116.5–117°; had a specific rotation $[\alpha]_D^{25}$, –35° and c = 1.0 in chloroform, and was not depressed in melting point by authentic cadinene hydrochloride.

Fraction 26 had a molecular refraction R_D = 66.5 corresponding to a bicyclic sesquiterpene with two double bonds. From 4 Gm. of oil 2.9 Gm. of crude hydrochloride was prepared. The hydro-

chloride melted at 85–87° after several alternate recrystallizations from ethanol and hot acetic acid.

Anal.—Calcd. for $C_{15}H_{26}Cl_2$; C, 64.97; H, 9.45. Found: C, 65.35; H, 9.17.

From the recrystallization behavior it seems possible that two hydrochlorides were formed. The same behavior and the same hydrochloride was obtained from a more pure sample of the sesquiterpene isolated from the heavy oil. This sample had the following properties: d_4^{25} , 0.915; n_D^{25} , 1.5051; $[\alpha]_D^{25}$, –50.3; b_{12} , 130°; and R_D , 66.1. One gram of the purified bicyclic sesquiterpene was mixed with 150 mg. of 5% palladium on charcoal and heated five and one half hours at 135°. The catalyst was removed by suction filtration and the clear liquid was heated with an alcohol solution of 0.6 Gm. of trinitrobenzene at 100° for two minutes. Eighty-two hundredths gram of cadalene trinitrobenzene adduct was received. After two recrystallizations from alcohol the adduct melted at 111–112° and showed no melting point depression with authentic cadalene trinitrobenzene adduct.

To sum up, the light oil of *Pinus armandi* is composed of: *l*- and *dl*- α -pinene, 53.5%; *l*-camphene, 3%; *l*- β -pinene, 5%; *l*-limonene, 21%; *n*-undecane, about 0.7%; *l*-bornyl acetate, 5.5%; a bicyclic sesquiterpene, b_{12} 116–118°, 2.4%; a bicyclic sesquiterpene related to cadalene 3.0%; pot residue and loss 5.9%.

THE HEAVY OIL OF *P. ARMANDI*

A batch of 140 Gm. of the heavy oil of *P. armandi* oleoresin was distilled through a 3-inch long Vigreux column with reflux ratio 2:1 and pressure of 1 mm. of mercury. The results of the distillation are shown in Table III.

Fractions A, B, C, D, and E were redistilled through a Todd, 5-mm. inside diameter, 90 cm. long, wire-spiral column at a 5:1 reflux ratio. The composition was about the same as Fractions 16 to 26 of the light oil from *P. armandi* oleoresin. The first fractions were mainly *l*-bornyl acetate. About 6 Gm. of *l*-bornyl acetate was crystallized from the appropriate fraction. After recrystallization from hexane the bornyl acetate melted at 26.5–27.5°, and showed no depression in melting point by admixture with an authentic sample.

The remainder of Fractions A, B, C, D, and E was mainly composed of two sesquiterpenes with the sesquiterpene of Fraction 26 in the light oil predominating. It was found in larger quantity and in higher purity than in the light oil. This purified bicyclic sesquiterpene had the same sesquiterpene hydrochloride as Fraction 26 of the light oil.

It is estimated that Fractions A, B, C, D, and E combined, contained 20% *l*-bornyl acetate; 14% of the same sesquiterpene as was found in Fraction 21 of the light oil; 58% of a cadalene type bicyclic sesquiterpene corresponding to the sesquiterpene of Fraction 26 of the light oil, and about 8% of the higher boiling constituents.

The Fractions F, G, H, and I crystallized on standing a few weeks in the refrigerator. About 5 Gm. of crystals were removed by filtration at reduced pressure. After purification by sublimation, followed by recrystallization from petroleum ether, the crystals melted at 137–137.5°. The literature value for albicaulol is 135° (3). A mixture with some

albicaulol from *P. albicaulis* turpentine showed no depression in melting point. The albicaulol from *P. armandi* had the properties: $[\alpha]_D^{25}$, -103.8 ; $c = 4.3$ in chloroform; a strong band at 3.2μ in the infrared corresponding to a secondary or tertiary OH group; no appreciable absorption maxima in the ultraviolet between 220 and 300μ . The alcohol may be the optical antipode of sesquigoyol (6) which has similar properties. The alcohol "lambertol" (4) which occurs in *P. lambertiana*, also a white pine, melts at 133° which is lower than the values for the other mentioned sesquiterpene alcohols; and it may be identical with these.

After two crops of albicaulol were removed from Fractions F, G, H, and I, the mother liquor was kept several weeks at 0° and crystals of a second substance formed. This substance was a diterpene hydrocarbon with the following properties: crystallized from ethanol at 0° , m. p. $58-59^\circ$; $[\alpha]_D^{25}$, $+238$; $c = 1.42$ in chloroform; the crystals autoxidized after several days standing at room temperature.

Cembrene, a diterpene which melted at $58-59^\circ$, had previously been isolated from *P. albicaulis*. For comparison, a sample of cembrene was isolated from a sample of a high-boiling fraction of *P. albicaulis* turpentine by crystallization from ethanol at 0° . The cembrene had the following properties: m. p. $58-59^\circ$; $[\alpha]_D^{25}$, $+239$; $c = 2.15$ in chloroform.

A mixed sample of the diterpene from *P. armandi* and cembrene from *P. albicaulis* melted at $58-59^\circ$. The diterpene thumblelene previously isolated by Sebe (6) has the following properties: m. p. $59-60.5^\circ$; $[\alpha]_D^{25}$, $+230.2$; readily autoxidized on standing several days exposed to the air. Thumblelene is probably the same diterpene as the one found in *P. armandi* and *P. albicaulis*.

About 9 Gm. of cembrene was filtered from the mother liquor by repeated seeding and crystallization at 0° .

One gram of the mother liquor from which the cembrene had crystallized was heated at 100° for 30 minutes with 0.36 Gm. of maleic anhydride. The crude product was washed with 10 ml. of hexane and about 0.3 Gm. was received. The adduct melted at $148-149^\circ$ after two recrystallizations from hexane.

Anal.—Calcd. for $C_{24}H_{34}O_3$: C, 77.79%; H, 9.25%. Found: C, 78.03%; H, 9.76%. Since a similar compound was not produced from the cembrene by similar treatment, it is evidently a derivative of a second diterpene hydrocarbon.

Judging from the above-presented data, the composition of the heavy oil of *P. armandi* is estimated to be: 12.5% *l*-bornyl acetate; 8-9% a bicyclic sesquiterpene; b_{12} $116-118^\circ$; 36% a bicyclic sesquiterpene related to cadalene; albicaulol, 8%; cembrene, 25%; a diterpene which gives a maleic anhydride adduct, 5%; tails, 1%; pot residue and loss, 4%.

Pinus bungeana Zuc. is a mountain pine of central China; Shansi and in neighboring parts of Shensi and Hopei and as far south as the province of Hupeh. Systematically, *P. bungeana* is grouped with *P. gerardiana* of the northwestern Himalayas and northeastern Afghanistan. It is a picturesque pine, widely planted by Chinese in the vicinity of temples and in cemeteries.

Commercial turpentine of *P. gerardiana* was analyzed by Simonsen and found to consist of about 78% *d*- α -pinene; about 7% *d*- β -pinene,² and about 12% of sesquiterpene, which did not yield any solid derivatives. There was a small amount of an unidentified sesquiterpene alcohol; tests for phellandrene, dipentene, terpinene, and terpineol were negative.

It was impossible to procure oleoresin of *P. bungeana* from China, so we obtained a sufficient amount of it from two trees cultivated in California. We had previously found that chemical composition of turpentine does not change when a pine is transplanted from one part of the world to another. It is deemed safe, therefore, to report on composition of *P. bungeana* turpentine obtained from the trees cultivated in California.

The turpentine was distilled from the oleoresin (which was semisolid and crystalline) under reduced pressure so that at the end of the operation the temperature was 190° and the pressure was 0.1 mm. of mercury. The pot residue (rosin) was very hard and brittle, which showed that all volatile fractions (including possible sesquiterpenes) had been removed.

TABLE II.—PHYSICAL CHARACTERISTICS OF *P. BUNGEANA* TURPENTINE

Origin of Sample	Yield of Oleoresin, %	Density, d_{4}^{25}	Index of Refraction, n_D^{25}	Specific Rotation, $[\alpha]_D$	Amount of Turpentine, Gm.
Chico, Calif. ^a	25	0.8625	1.4730	- 7.0	40
Placerville, Calif.	27	0.8627	1.4745	-11.0	105

^a Thanks are due to Mr. L. E. Jolly, in charge of Chico Plant Introduction Garden for furnishing the material.

The two samples were mixed and a batch of 135 Gm. was fractionated at atmospheric pressure in a 15-mm. inside diameter, 90-cm. long Todd column packed with glass helices; a 10:1 reflux ratio was maintained. Results of the fractional distillation are shown in Table III. The residue boiling above 166° was redistilled at 10 mm. of pressure in a small flask equipped with a 6-inch Vigreux-type column. More than one half of the material (4 Gm.) distilled at $60-62^\circ$. This fraction A possessed the following properties: density, $d_4^{25} = 0.8599$; index of refraction, $n_D^{25} = 1.4780$; specific rotation, $[\alpha]_D = -18.6$. Apparently this fraction consisted chiefly of β -pinene. The rest of the material (3 Gm.) consisted of higher boiling ingredients, probably sesquiterpenes. Because of the small amount of this higher-boiling material, we were unable to investigate it.

Friction 2 of *P. bungeana* was tested for presence of α -pinene. From 7 ml. of oil, 1.4 Gm. of *dl*- α -pinene nitrosochloride melting at $104-104.5^\circ$ was prepared. When mixed with authentic *dl*- α -pinene nitrosochloride it showed no depression of the melting point.

From a portion of the nitrosochloride, *dl*- α -pinene nitrolpiperidide melting at $120-121^\circ$ was

² Generally, β -pinene is levorotatory.

TABLE III.—FRACTIONAL DISTILLATION OF TURPENTINES OF
PINUS ARMANDI AND P. BUNGEANA

Fractions	Pressure, mm.	Boiling Range, °C.	Distillate	Density, d ₄ ²⁴	Index of Refraction, n _D ²⁴	Specific Rotation, [α] _D ²⁴
<i>Pinus armandi</i> —Light Oil (745 Gm. Used)						
1	12	42	37.8	0.854	1.4643	— 1.9
2	12	42	15.6	0.855	1.4647	— 10.8
3	12	42-44	1.7	0.860	1.4682	— 34.5
4	12	44-46	1.0	0.860	1.4711	— 36.2
5	12	46-49	1.2	0.857	1.4731	— 29.6
6	12	49-53	1.8	0.851	1.4731	— 20.1
7	12	53-55	1.1	0.843	1.4716	— 23.2
8	12	55-58	5.1	0.840	1.4714	— 61.2
9	12	58-59	9.4	0.837	1.4718	— 100.0
10	12	59-60	7.4	0.838	1.4719	— 116.0
11	12	60-67	0.1	0.840	1.4744	— 88.9
12	12	67-71	0.1	0.844	1.4733	— 29.4
13	12	71-88	0.9	0.808	1.4472	— 5.3
14	12	88-96	0.03	0.835	1.4321	— 13.6
15	12	96-98	0.6	0.923	1.4552	— 31.0
16	12	98-99	0.9	0.966	1.4604	— 38.8
17	12	99-100	2.8	0.973	1.4611	— 39.6
18	12	100-106	0.9	0.962	1.4658	— 34.6
19	12	106-110	0.3	0.945	1.4719	— 26.0
20	12	110-114	0.4	0.927	1.4784	— 18.5
21	12	114-116	0.5	0.910	1.4854	— 9.0
22	12	116-118	0.6	0.902	1.4907	— 5.1
23	12	118-122	0.9	0.900	1.4939	— 8.7
24	12	122-128	0.9	0.904	1.4993	— 19.0
25	12	128-131	0.6	0.907	1.5021	— 45.4
26	12	131-134	1.5	0.911	1.5041	— 60.4
Residue and Losses			5.87			
<i>Pinus armandi</i> —Heavy Oil (140 Gm. Used)						
A	1	75-80	13.5	0.9370	1.4823	— 33.9
B	1	80-85	15.9	0.9185	1.4951	— 32.6
C	1	85-90	9.7	0.9138	1.5007	— 33.6
D	1	90-100	13.7	0.9138	1.5038	— 27.0
E	1	100-110	9.7	0.9138	1.5068	+ 2.4
F	1	110-120	1.1			
G	1	120-128	3.8			
H	1	128-130	24.8			
I	1	130-140	2.9			
J	1	140-160	0.9			
Residue and Losses			4.0			
<i>Pinus bungeana</i> (135 Gm. Used)						
1	758	156-157	0.7	0.8571	1.4664	+ 2.7
2	758	157-158	24.3	0.8570	1.4669	+ 3.0
3	758	158-159	17.9	0.8574	1.4686	— 2.7
4	758	159-160	8.5	0.8586	1.4686	— 4.1
5	758	160-161	8.2	0.8600	1.4709	— 6.5
6	758	161-162	3.7	0.8640	1.4723	— 10.0
7	758	162-163	5.6	0.8640	1.4734	— 11.3
8	758	163-164	6.7	0.8640	1.4750	— 16.5
9	758	164-165	5.6	0.8640	1.4763	— 20.0
10	758	165-166	6.7	0.8657	1.4769	— 21.7
Residue Loss		Above 166	5.6	0.8841	1.4878	

prepared. On admixture of an authentic sample of *dl*- α -pinene nitropiperidine no melting point depression was observed.

The physical properties of Fractions 3 to 8 indicated that they were mixtures of α - and β -pinenes, gradually getting close to those of β -pinene at Fraction 9. From 10 Gm. of Fraction 9, 0.52 Gm. of nopinic acid was prepared. After one recrystallization from benzene, it melted at 125-126° and was not depressed in melting point by admixture of an authentic sample of nopinic acid.

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