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CHEMICAL COMPOSITION OF *P. ELLIOTTII* VAR. *ELLIOTTII* TURPENTINE AND ITS POSSIBLE RELATION TO TAXONOMY OF SEVERAL PINE SPECIES

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Abstract—The botanical complexity of *Pinus elliottii* is briefly reviewed; chemical composition of turpentine of this species has been studied extensively but not completely. The present investigation revealed the following composition of *P. elliottii* var. *elliottii* turpentine: α-pinene, 56·6%; camphene, 0·6%; β-pinene, 35·6%; myrcene, 0·3%; dipentene, 1·5%; β-phellandrene, 3·3%; *p*-cymene 0·2%; methyl chavicol, 0·7%. Camphene, myrcene and *p*-cymene are reported for the first time as constituents of *P. elliottii* var. *elliottii* turpentine.

The difference of turpentine composition between var. *elliottii* and var. *densa* and chemical relation of *P. elliottii* to other pine species are discussed. The possible relationship of the Caribbean pines is suggested; further studies appear to be necessary.

INTRODUCTION

Pinus elliottii Engelmann, called slash pine, grows from southern South Carolina through southern parts of Alabama and Mississippi to southeastern Louisiana. To the South its area extends through southeastern Georgia to central Florida (Fig. 1).

The botanical history of *P. elliottii* is long and complicated. Originally it was described as *Pinus teeda* L. var. *heterophylla* Elliott.[1] Later it became known as *P. Elliottii* Engelmann.[2] Both Sudworth[3] and Shaw[4] included it in *P. caribaea* Morelet. Little and Dorman[5,6] restored the name *P. elliottii* Engelmann to the slash pine of the southeastern United States and also described the slash pine of southern Florida as *P. elliottii* variety *densa* Little & Dorman. By virtue of this rearrangement, American slash pine became a species independent of *P. caribaea* Morelet of the Caribbean Islands and Central America.

As the variety *densa* was added by Little and Dorman to the typical *P. elliottii*, the rules of botanical nomenclature (Art. 25, 8th Int. Bot. Congr., Paris, 1924) demanded that the typical *P. elliottii* become known as *P. elliottii* var. *elliottii.* If, in the future, *P. elliottii* var. *densa* is given a rank of an independent species (which is possible) the change would also affect the nomenclature of the typical *P. elliottii* in that its varietal epithet "*elliottii*" would automatically cease to exist.

Little and Dorman[5] tabulated morphological differences between *P. elliottii* var. *elliottii* and *P. elliottii* var. *densa.* The most interesting morphological character of the *densa* variety

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[1] S. ELLIOTT, *Sketch of the botany of South Carolina and Georgia*, Vol. 2. J. R. Schenk, Charlston (1824).

[2] G. ENGELMANN, *Acad. Sci.* San Louis. Trans. **4**, 161 (1880).

[3] G. B. SUDWORTH, *Torrey Botan. Club. Bull.* **20**, 40 (1893).

[4] G. R. SHAW, *Publ. Arn. Arb.* **5** (1914).

[5] E. L. LITTLE, JR. and K. W. DORMAN. U.S. Forest Service. *S-E. For. Exp. Sta. Paper* No. 36, 82 (1954).

[6] E. L. LITTLE, JR. and K. W. DORMAN. *J. Forestry* **50**, 918 (1961).

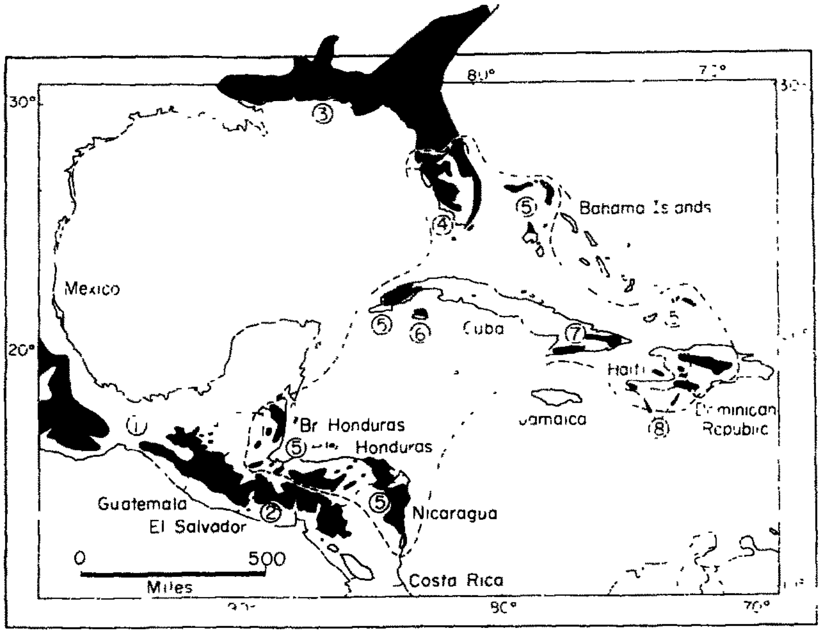

FIG. 1. DISTRIBUTION OF THE GENUS *Pinus* IN THE CARIBBEAN AREA.

------General area of Caribbean pines

■— Forest areas

(1) Pine forests of Mexico
(2) Pine forests of inner Central America
(3) Area of *Pinus elliottii* var *elliottii*
(4) Area of *P elliottii* var. *densa*

(5) Occurrence of *P. caribaea*
(6) Occurrence of *P. tropicalis*
(7) Occurrence of *P. cubensis*
(8) Occurrence of *P. occidentalis*

Map is modified from W. M. DENEVAN, *Univ. of Calif. Publ. Geography*. **12**, 251 (1961)

is the so-called "grass stage" of its seedlings, characterized by very short stem, many crowned needles, thick hypocotyl, and thick tap root. "Grass stage" is also found in *P. palustris*, a species of the southwestern United States, *P. tropicalis* of Cuba, *P. montezumae* of Mexico and some other Mexican pines and (subject to verification) in *P. merkusii* of Burma and Viet Nam, but not of Sumatra. Although *P. elliottii* has been crossed artificially with *P. palustris*, no natural hybrids between these two species have been reported; it is possible, however, that occasionally they do intercross. According to personal communication of Dr. A. E. Squillace of the U.S. Forest Service, there are no experimental indications of *P. elliottii* var. *elliottii* crossing naturally with *P. elliottii* var. *densa*.

EARLY CHEMICAL INVESTIGATIONS

P. elliottii var. *elliottii* (together with *P. palustris*) has been the chief source of "Naval Stores" (i.e. rosin- and turpentine for industrial purposes). Accordingly chemistry of its turpentine has been studied by many investigators.

The turpentine of *Pinus elliottii* var. *elliottii* (referred to as *P. heterophylla* Sudw.) was analyzed in 1929 by Dupont and Barraud.[7] The product was obtained from the Hercules Powder Company. Physical constants of the turpentine were: Density, $d^{25} = 0{\cdot}8533$; index

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[7] G. DUPONT and M. BARRAUD, *Procès-verbaux Soc. Sci. Phys. Natur. Bordeaux, Année 1928* 29 15 (1930).

of refraction, $n^{25} = 1{\cdot}4631$; optical rotation $\alpha_j = -30{\cdot}78°$. The turpentine contained: 1-α-pinene, 75·6%; 1-β-pinene, 21·2%; and tails, 3·2%.

In 1932 Palkin[8] reported the following data for fresh gum slash pine turpentine: Density, $d_4^{15\cdot6} = 0{\cdot}8657$; index of refraction, $n_D^{25} = 1{\cdot}4694$; optical rotation, $\alpha = -25{\cdot}58°$; The composition of this turpentine was as follows: 1-α-pinene, 61%; 1-β-pinene, 33·7%; and tails, 5·3%.

Chadwick and Palkin[9] reported that the tails of slash pine turpentine contained dipentene, methyl chavicol, and very little of alcohols, esters, and others other than methyl chavicol. Possibly some components of the higher fractions (tails) were of a secondary origin.

Further investigations at the U.S.D.A. Naval Stores Laboratory, Olustee, Florida revealed presence of varying amounts of β-phellandrene (detected and identified by vapor phase chromatography methods) in the turpentine samples taken from individual trees of *P. elliottii* var. *elliottii*.[10]

EXPERIMENTAL

In 1962 we obtained a large composite sample of *P. elliottii* var. *elliottii* oleoresin gathered from a group of 400 trees near Olustee, northern Florida. These trees were a part of an experiment of inducing flow of oleoresin and their wounds were sprayed for this purpose with a 2 per cent solution of an amine salt of 2,4-dichlorophenoxyacetic acid ("2,4-D").

A batch of 3763 g of oleoresin was distilled at 30 mm pressure with the distillate coming over between 27° and 180°. At the end the distillate was removed, the pressure was lowered to 1 mm and the rest of the turpentine was distilled by raising the temperature to 218°. Both turpentine fractions were combined.

Results: water, 185·8 g; turpentine, 777·3 g; rosin, 2510·0 g; Constants of turpentine: Specific rotation $[\alpha]_d^{25}$ $-26{\cdot}60$; index of refraction $n_d^{23\cdot5}$ 1·4688, density d_4^{25} 0·8639.

A portion of 714 g of turpentine was fractionated using a Todd fractionating column (Stedman packing) at a reduced pressure[11] (Table 1). Each fraction was qualitatively analyzed by vapor phase chromatography using Ucon column[11] and the fractions of similar composition were combined. The physical constants of those combined fractions were determined (Table 1), and each was quantitatively analyzed by vapor phase chromatography using $\frac{1}{8}$ in. × 6 ft β,β-oxydipropionitrile 10 per cent on acid-washed chromosorb column 60/80[12] (Table 2). (Aerograph Hy-Fi A-600-B instrument; flow rates, N_2—15 ml/min, H_2—15 ml/min; oven temperature 65°; injector temperature −80°. Otherwise as with Ucon column.)

Methyl chavicol was identified by preparation of anisic acid (m.p. 181–2°), and β-phellandrene by preparation of nitrosite (m.p. 97·5°); neither melting point was depressed upon admixture of a respective authentic substance. α-Pinene and β-pinene were preparatively characterized by previous workers.[7] The rest of the constituents occurred in too small amounts for preparation of derivatives and was characterized by Ucon and β,β-oxydipropionitrile VPC data only. The relative retention volumes obtained were identical to those of authentic terpenes used for comparison; both approximated closely the published data.[11,12]

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[8] S. Palkin, *U.S. Dept. Agr. Tech. Bull. 276* (1932).

[9] T. C. Chadwick and S. Palkin, *U.S. Dept. Agr. Tech. Bull. 749* (1941).

[10] Unpublished information supplied by Dr. Gordon S. Fisher, head of the Turpentine Division, U.S.D.A. Naval Stores Laboratory, Olustee, Florida.

[11] N. T. Mirov, E. Zavarin and J. G. Bicho, *J. Pharm. Sci.* **51**, 1131 (1962).

[12] M. H. Klouwen and R. ter Heide, *J. Chromatog.* 3, 297 (1962).

TABLE 1. PHYSICAL CONSTANTS OF FRACTIONS FROM *Pinus elliottii* TURPENTINE

Fraction	Percentage	Boiling point (°C)	Column pressure (mm Hg)	Density d_4^{25}	Refractive index n_D^{25}	Specific rotation $[\alpha]_D^{25}$
A	32·20	73–74	49–50	0·8578	1·4623	−32·20
B	45·40	74–80	49–50	0·8641	1·4682	−27·10
C	14·50	80–83	49–50	0·8650	1·4746	−21·38
D	0·65	83–87	50	0·8580	1·4761	−16·85
E	1·00	87–90	50	0·8576	1·4800	−15·75
F	1·60	90–91	50	0·8550	1·4835	−11·91
G	0·90	91–91·5	52	0·8435	1·4858	−9·33
H	0·80	91·5–92·5	53	0·8389	1·4846	−8·34
I	1·15	92·5–97	53	0·8394	1·4831	−9·24
J	0·75	up to 112	3·5	0·8465	1·4966	−4·28
K	0·40	112–225	3·5	0·9566		
Residue	0·65	—	—			

TABLE 2. COMPOSITION OF THE *Pinus elliottii* TURPENTINE

Fraction*	Percentage†	α-Pinene	Camphene	β-Pinene	Myrcene	Dipentene	β-Phellandrene	*p*-Cymene	Unknown‡ terpene	Methyl chavicol	Unknown sesquiterpene
		Per cent†									
A	32·20	99·0	0·5	0·5							-
B	45·40	53·5	1·0	45·5	-						
C	14·50	3·5	—	96·5	-	--	-	-			
D	0·65		---	81·5	15·5	1·0	1·5	0·5	—		-
E	1·00	--	—	26·0	16·0	16·0	32·5	2·5	7·0		
F	1·60	--		2·0	2·5	20·4	70·6	2·0	2·5		-
G, H	1·70	—	--	tr	-	37·2	61·3	1·5		-	-
I	1·15	—		tr	-	32·6	64·7	2·7	·		—
J	0·75	--		---		8·0		7·0		66·0	19·0
K	0·65	-		-		--				49·0	51·0
Residue	0·65	-	-	-	-						
Total†		56·6	0·6	35·6	0·3	1·5	3·3	0·2	0·1	0·7	0·5

* As in Table 1.

† The per cent figures of the second column and of the totals refer to the total turpentine, the rest of the figures refer to the individual fractions.

‡ Relative retention volume (α-pinene = 1·00) (at 76°, Ucon column, 15 ml/min nitrogen flow) is equal to 2·1; the peak appears right after myrcene.

Camphene, myrcene, and *p*-cymene are reported for the first time as constituents of *Pinus elliottii* turpentine. Dipentene and methyl-chavicol were reported previously by Chadwick and Palkin[9] on the basis of physical constants of respective fractions only.

Table 2 shows that, disregarding traces of camphene, myrcene, *p*-cymene and sesquiterpenes, the composition of *P. elliottii* var. *elliottii* turpentine was found to be about the same as reported by Chadwick and Palkin[9] except for β-phellandrene, which was not mentioned by them. In our investigation this compound comprised 3·3 per cent of the turpentine, i.e. quite close to the data obtained by Dr. Fisher[10] who found that two-thirds of all *P. elliottii* trees contained at least 5 per cent of this terpene.

It is not clear how Chadwick and Palkin overlooked β-phellandrene in their thorough investigation of *P. elliottii* turpentine. It is possible that they used material previously stored in partly filled containers exposed to light or that they mistook β-phellandrene for dipentene. It is, however, more reasonable to assume that they obtained their material from a locality where *P. elliottii* var. *elliottii* contained either no β-phellandrene, or only traces. They did not say from where their product had come, but it may have been from parts to the north, possibly Georgia. Dr. Fisher's samples of *P. elliottii* var. *elliottii* turpentine on the other hand all came either from northern or central Florida, i.e. from the southern part of its range.

DISCUSSION

It is seen that our knowledge of occurrence of β-phellandrene in *P. ellitotii* var. *ellitotii* is yet too scanty to be applied for drawing any definite taxonomic conclusions. Presence of varying and, on the average, apparently small quantities of phellandrene in turpentine of the typical *P. elliottii* is intriguing. To understand the significance of the presence of β-phellandrene in *P. elliottii* var. *elliottii* turpentine, it is expedient to inquire into the geographic distribution of β-phellandrene of the whole genus *Pinus*. 1-β-Phellandrene is a monocyclic terpene; it occurs chiefly in pine species of western America, Mexico, and to a lesser degree in the pines of southwestern Asia. Generally, it is found in quantities sufficient to be isolated by conventional methods of fractional distillation and identified by subsequent preparation of crystalline β-phellandrene nitrosite.

On the other hand, pine species of eastern North America (with exception of *P. elliotti*) do not contain 1-β-phellandrene in their turpentines. Traces of this terpene might be detected by vapor chromatography, but not in quantitites that would make possible its positive identification.

P. elliottii var. *densa* does contain 1-β-phellandrene in its turpentine. In one composite sample from the southern part of Florida (Fort Myers) as much as 19 per cent of this terpene was found.[13] *P. caribaea* from the Caribbean Coast of Central America (Nicaragua) also contains 1-β-phellandrene.[14] Incidentally, *P. caribaea* turpentine from Nicaragua was found also to contain considerable quantities of Δ^3-carene and of longifolene, both quite common components of turpentines of western American and Mexican pine species. Δ^3-Carene was also found in turpentine of *P. occidentalis* of Hispaniola.

To sum up, *P. elliottii* var. *densa* has chemical affinity both with *P. elliottii* var. *elliottii* and with *P. caribaea*; on the other hand, *P. elliottii* var. *elliottii* has no such affinity (i.e. presence of identifiable quantities of 1-β-phellandrene) with any northern pine species of eastern North America.

P. caribaea is definitely related chemically to many Mexican and western American, but to none of the eastern American pine species. Could it be, then, that *P. elliottii* var. *densa* is not an eastern American pine migrated to southern Florida from the North, as apparently generally supposed, but rather a Caribbean species whose tertiary ancestors migrated from western America to Mexico and Central America and from there to the Caribbean islands?

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[13] N. T. Mirov and P. M. Iloff, Jr., *J. Am. Pharm. Assoc., Sci. Ed.* **45**, 629 (1956).

[14] P. M. Iloff, Jr. and N. T. Mirov, *J. Am. Pharm. Assoc., Sci. Ed.* **43**, 738 (1954).

Historical geography of the Caribbean pines and the possible routes of their migration in that area are discussed by Little and Dorman.[5] It suffices to add here that intermittent land bridges between Central America and the Caribbean islands existed during the first part of the Tertiary Period as shown by Schuchert.[15] These bridges apparently served as paths of migration of pines from the continent to the Caribbean area. On the other hand, southern Florida has never had land connexions with the Antilles.

Southern Florida is now separated from the Bahamas with a stretch of water only 60 miles wide; from Key West, Florida to Cuba the distance is not greater than one hundred miles. When the southern part of Florida emerged above the water in the Pleistocene and thus became available for colonization by pines, the distances between the peninsula and the Caribbean islands was not much greater than now. Pine seeds could have been carried easily from the islands to the mainland by hurricanes. Little and Dorman[5] said "it is not known in which direction migration [of pines] has occurred" in the Caribbean area, i.e. from the American mainland southward or from the Antilles to the mainland. General migration routes for the genus *Pinus* since its Mesozoic incipience have been from the north southward, but reversed migrations from the south northward, although of a local character, also have occurred during the paleobotanical history of the genus. Cretaceous reversed migration in eastern North America was mentioned by Berry.[16] During the Tertiary Period some pines advanced north in the southwestern part of the United States. Migration of *P. insularis* and *P. merkusii* from the mainland of the southeastern Asia to the Philippines via Sumatra and then northward occurred at the beginning of the Quaternary. Such may have been the quaternary migration of *P. elliottii* var. *densa*, or rather its predecessor, from the Antilles to Florida.

In the light of our present knowledge of the relationship of the southern Florida pine, it is of course difficult to say whether it is a pine of the southeastern United States or should be considered a Caribbean species. Has it migrated to Florida from the north or from the Antilles? Is it a variety of *P. elliottii* or of *P. caribaea*? Perhaps it should be considered an independent species. Where has it acquired its β-phellandrene - from *P. elliottii* or from *P. caribbea*?

A more thorough investigation of geographic and taxonomic distribution of l-β-phellandrene in the whole area of *P. elliottii* and *P. caribaea* is desirable. A study of this nature offers a possibility of applying a chemical method to a taxonomic problem of a small group of species and thus of contributing to this, still inadequately documented subject. Other Caribbean pines also should be chemically studied. Presence of Δ^3-carene in *P. occidentalis*[11] suggests its affinity with some pines of Central America (Mexico); turpentine composition of *P. cubensis* Grisebach, a species of eastern Cuba closely related to *P. occidentalis*, should be ascertained. A thorough chemical investigation of pines in the Caribbean area and in the southeastern United States may not only help to understand better the taxonomic position of southern Florida slash pine, but may also contribute to solving the major problem of occurrence and migration of pines in the Caribbean area.

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[15] C. Schuchert, *Atlas of Paleographic maps of North America*, with an Introduction by C. O Dunbar Wiley, N.Y. (1955).

[16] E. W. Berry, *U.S. Geol. Survey, Profess. Papers* No. **156**.