treated with approximately 5 ml. of 0.1 *N* barium hydroxide solution to precipitate any carbonate. The solution is brought to boiling, filtered from carbon and barium carbonate, acidified with 50% sulfuric acid and the HCN^{15} distilled over into 20 ml. of 0.1 *N* sodium hydroxide. Ordinary sodium cyanide may then be added to this to obtain a solution of the desired normality or atom per cent. excess N^{15}.

Four preparations were carried out using ordinary potassium phthalimide, and yields of 97–100% were obtained in each case.

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Terpenes in the Essential Oil of *Haplopappus laricifolius*, Gray[1]

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As part of a study of various essential oil plants of southern Arizona, some of the principal terpene constituents in the volatile oil of *Haplopappus laricifolius*, Gray were determined. The oil was obtained by steam distillation of the leaves and small stems of the plant, a resinous, perennial shrub found at 3000 to 6000 feet elevation. The yellow oil comprised about 0.6% of the fresh weight of plant material and had the following constants: d^{32} 0.8631, $n^{20}\text{D}$ 1.4842, $\alpha^{34}\text{D}$ −14.06°, acid no. 3.7, ester no. 7.8, and ester no. after acetylation, 40. The oil was fractionated *in vacuo* into 29 fractions; and by means of their physical constants and crystalline derivatives, certain fractions were shown to contain *dl*-α-pinene, *l*-β-phellandrene, and *l*-phellandral, making up, respectively, 20, 30 and about 1% of the whole oil. A more complete analysis will be presented in a future publication.

Table I

Physical Constants of Certain Fractions of Oil of *Haplopappus laricifolius*

Fract.	Pure compound (literature)	Press., mm.	Distn. temp., °C.	Wt., g.	Wt., %	$n^{20}\text{D}$	d^{30}_{15}
1b		19	58–60	3.8	2.38	1.4748	0.8542
2		19	60–62	16.9	10.58	1.4768	.8576
		700	157				
3		19	62–64	11.5	7.20	1.4788	.8558
	α-Pinene	20	52[a]			1.4670[b]	[b]
		760	155–156[b]				
5		19	66–68	18.4	11.51	1.4817	.8558
6		19	68–70	31.7	19.84	1.4835	.8488
		703	169–170				
	β-Phellandrene	24	78[c]			1.4826[d]	[d]
		758	178–179[c]				
18		0.25	64–68	0.7	0.44	1.4920	.9509
19		0.25	68–70	0.3	0.19	1.4929	.9509
	Phellandral	1.5	75[e]			1.4912[f]	[f]

[a] C. von Rechenberg's tables of boiling points at reduced pressures of isolates and synthetics, reproduced by Ernst Guenther, "The Essential Oils," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1948, p. 379. [b] F. H. Thurber and R. C. Thielke, This Journal, **53**, 1030 (1931); d^{20} 0.8590. [c] G. E. Smith and T. F. West, *J. Soc. Chem. Ind.*, **56**, 300 (1937). [d] P. A. Berry, *Australian Chem. Inst. J. Proc.*, 14, 376 (1947); $d^{15.5}_{15.5}$ 0.843. [e] R. G. Cooke and A. K. Macbeth, *J. Chem. Soc.*, 1408 (1938). [f] A. R. Penfold, *ibid.*, 121, 266 (1922); d^{20} 0.9412.

Experimental

The oil obtained by steam distillation was dried over anhydrous sodium sulfate prior to fractionation through a helix-packed column. The physical constants of the fractions were determined in the usual manner, and those for the fractions concerned are listed in Table I.

Fractions 1b, 2 and 3 were shown to contain α-pinene by preparation of the nitrosochloride, which showed no depression in its melting point[3] when mixed with the same derivative of an authentic sample of α-pinene, and by determination of the nitrogen percentage of the nitrosochloride, the preparation of which was carried out according to the method of Wallach.[4] After recrystallization six times from chloroform–methanol the final product was obtained in the form of colorless plates melting at 106–107°. The melting point of an equal mixture of the nitrosochlorides of fraction 2 and authentic α-pinene was also 106–107°.

Anal. Calcd. for $C_{10}H_{16}ClNO$: N, 6.94. Found: N, 6.98.

Fractions 5 and 6 were found to contain β-phellandrene by means of their physical constants and by preparation of the solid nitrosochloride and nitrosite. The former derivative was prepared in the same manner as was pinene nitrosochloride. The product was recrystallized twice from acetone as white prisms, m.p. 101.5–102°. Francesconi and Sernagiotto[5] reported m.p. 101–102°. The formation of this compound identifies the original constituent as the β-isomer, since, according to West,[6] the α-isomer does not form a solid nitrosochloride under the conditions employed here. This was also confirmed with an authentic sample of α-phellandrene[7] in this Laboratory. The presence of phellandrene was confirmed by the immediate formation of the solid nitrosite, prepared according to the test of Wallach and Gildemeister.[8]

l-Phellandral was identified in fractions 18 and 19 by preparation of the 2,4-dinitrophenylhydrazone and by determination of the nitrogen percentage of this derivative. The hydrazone was prepared in the usual manner and, after recrystallization from a 1:1 chloroform–ethanol solution, the product was obtained in the form of reddish-orange prisms which melted at 201–202°. Macbeth and Price[9] reported m.p. 202–203°.

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: N, 16.87. Found: N, 17.00.

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(3) All melting points uncorrected; determined on a Fisher–Johns block.

(4) O. Wallach, *Ann.*, **245**, 201 (1888); **270**, 181 (1892).

(5) L. Francesconi and E. Sernagiotto, *Gazz. chim. ital.*, **46** (I), 119 (1916).

(6) T. F. West, *J. Soc. Chem. Ind.*, **58**, 122T (1939).

(7) This sample kindly supplied by Fritzsche Brothers, Inc., New York, N. Y.

(8) O. Wallach and E. Gildemeister, *Ann.*, **246**, 282 (1888).

(9) A. K. Macbeth and J. R. Price, *J. Chem. Soc.*, 152 (1935).