ical (*4, 7*), and thus it is a good nucleophile able to attack carbon tetrachloride. Sosnovsky (*10*), in a discussion of the compound trichloromethanesulfenyl chloride, discusses the products which seem to result from this reaction.

A least-squares fit of the data for both the carbon disulfide-sulfur and the carbon tetrachloride-sulfur experiments gives straight lines whose slopes, using the equation

$$\log \epsilon/(1/T) = -\Delta H/2.303\ R \tag{1}$$

where ϵ is the solubility, yields heat of solution ΔH_s values of 3.68 ± 0.05 kcal/mol for carbon disulfide and 6.4 ± 0.1 kcal/mol for carbon tetrachloride. On the basis of the fit of the curves, the solubility ϵ of the carbon disulfide-sulfur solution can be calculated using the equation

$$\log \epsilon = (-8.07 \times 10^2/T) + 4.16 \tag{2}$$

for the temperature range 22–102° C, while for carbon tetrachloride-sulfur solutions it can be calculated using the equation

$$\log \epsilon = (-1.41 \times 10^3/T) + 4.58 \tag{3}$$

for the temperature range −20° to 131° C.

For liquid sulfur dioxide-sulfur, the ΔH and ϵ cannot be given because points do not lie on a straight line.

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Separation of Longifolene from Pine Oil

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Pine oil obtained from extractives of ponderosa pine (*Pinus ponderosa Laws*) stumps was fractionally distilled to separate longifolene. The components of each fraction were determined by gas chromatography.

The pine oil obtained from a commercial size run of ponderosa pine stumps was examined by gas chromatography and found to contain about 20% of a sesquiterpene (longifolene) (*1*) not usually present in pine oil from southern pine stumps. Removal or separation of this component was necessary to market a pine oil equivalent to those already on the market.

This study on the separation of the components of pine oil was carried out to determine the feasibility of separating longifolene from pine oil.

Table I shows the composition of the starting pine oil and of each fraction of the distillation. The composition of fractions 1–6 combined and of a commercial pine oil are also included in Table I. Fractions 1–6 account for approximately 70% of the pine oil and contain only a trace of longifolene in the 6th fraction. Thirty-four percent of the longifolene is in fraction 7 and the remaining 66% in the pot residue. A bulb-to-bulb distillation of the residue gave longifolene of 98% purity.

EXPERIMENTAL

One drum of pine oil containing 336 lb was charged and distilled. The distillation column was 316 stainless steel, 5.75 in. i.d. with a 13-ft section packed with 1-in. pall rings. The charge was at total reflux for 1.5 hr prior to distillation. The pine oil was distilled at a 10:1 reflux ratio. Product temperature was maintained at 40–50° C to prevent crystallization of high-melting components such as borneol. An operating differential pressure of 25 mm Hg with 50 mm Hg top column pressure was maintained throughout the distillation. When the operating differential pressure began to drop, the run was stopped and the residue remaining in the pot removed.

Seven fractions weighing 35 lb each were taken and 53 lb of pot residue recovered. Approximately 38 lb were unaccounted for and assumed to have been carried over in the vacuum system. Each fraction, the pot residue, and the original pine oil were analyzed by gas chromatography. An F&M Model 700 gas chromatograph with dual columns and flame detector was used. The column was a 15-ft by $^3/_{16}$-in. copper column packed with 5% Versamid 900 on 70/80 mesh diatoport S. The column temperature was 150° C, and the helium flow 100 ml/min. The peak areas were measured with a disc integrator equipped with an automatic printer.

The pine oil components were identified by comparison of retention times with known compounds and by collecting and recording the infrared spectra of the individual peaks. The infrared spectrum of longifolene is in Figure 1, and the infrared spectra of 11 other pine oil components are deposited with the ACS Microfilm Depository Service (*2*).

SUMMARY

Longifolene was separated from other pine oil components using commercial equipment available in most plants. The distilled pine oil contains the same components in approxi-

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Table I. Composition of Pine Oil and Distillation Fractions

	Components	Rrt[a]	Whole pine oil	Fraction C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8[b]	C-(1-6)[c]	Commercial pine oil
1	α-Pinene	0.18	0.4	0.6	...	...	...	...	...	...	...	0.3	0.6
2	Δ^3-Carene	0.21	Tr[d]	2.4	...	...	...	...	...	...	...	0.2	...
3	Limonene	0.23	Tr	0.3	...	...	...	...	...	...	...	0.1	0.3
4	β-Phellandrene	0.25	Tr	0.9	...	...	...	...	...	...	...	...	Tr
5	?	0.26	Tr	1.3	...	...	...	...	...	...	...	...	1.7
6	?	0.30	Tr	1.1	...	...	...	...	...	...	...	0.6	
7	?	0.36	0.3	0.2	...	...	...	...	...	...	...	...	
8	?	0.37	Tr	2.0	...	...	...	...	...	...	...	0.1	2.8
9	?	0.40	0.3	1.3	0.1	...	...	...	...	...	...	0.5	
10	?	0.43	Tr	...	0.8	0.1	...	...	...	...	...	0.6	
11	?	0.49	1.7	...	16.2	3.5	...	...	...	...	...	0.6	1.1
12	Dihydro-α-terpineol	0.51	4.1	9.0			...	...	...	...	...	5.1	5.6
13	Terpinene-4-ol	0.52	7.5	12.2	...	...	3.1	...	...	...	...	8.6	9.8
14	β-Terpineol	0.55	7.9	...	14.5	4.2		...	...	...	...	9.4	5.1
15	Dihydro-β-terpineol	0.57	1.1	57.0	27.8	12.9		0.2	0.8	0.9	...		
16	Isoborneol	0.61	2.5				...	...	...		...	0.7	Tr
17	α-Terpineol	0.71	41.8	6.1	23.8	57.5	82.6	93.7	94.9	23.6	0.3	60.6	64.9
18	Borneol	0.80	11.3	5.6	16.9	21.8	14.3	6.1			2.2	12.0	8.1
19	?	0.91	0.6	0.3	...	...	...		2.9	10.5		...	...
20	Longifolene	1.00	20.3	...	...	...	...	...	1.4	65.1	83.2	...	...
21	*cis*-Anethole	1.18	0.3	...	...	...	...	...	...	...	6.1	...	Tr
22	?	1.31	...	...	...	...	...	...	...	...	2.9	...	...
23	*trans*-Anethole	1.42	...	...	...	...	...	...	...	...	4.4	...	...
24	?	1.55	...	...	...	...	...	...	...	...	1.0	...	...

[a] Relative retention time—relative to longifolene. [b] C-8 is the pot residue. [c] Fractions 1–6 combined. [d] Trace values less than 0.1%.

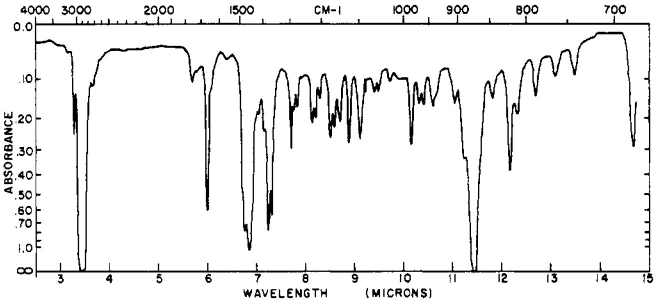

Figure 1. Longifolene

mately the same ratio as commercial pine oil from southern pine stumps. The last distillation fraction and the residue contain a concentrate of longifolene that can be redistilled to give the pure sesquiterpene.

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