have found the apparatus shown in Fig. I to be quite satisfactory.

The precipitate is susceptible to oxidation and must be kept away from air during drying. Also, the fact that high temperature will char the soap limits the drying temperature to about 80° C. The precipitate may be dried in a desiccator connected by a long rubber tubing to a source of hydrogen or carbon dioxide, and to a vacuum pump. After introducing the precipitate to be dried, the desiccator may be placed in a low-temperature steam drying oven for 3 hours.

The results obtained by the use of the insoluble-soap method and the data from which these results were computed, are compiled in Table II. In calculating the results for this table it was decided to accept the weight of the dried insoluble soap as representative of the weight of wood oil present in the sample, since the error of this assumption was considered to be within the limits of error of the method.

Although neither of the above methods has proved entirely satisfactory as a method for the estimation of wood oil in rosin varnishes, the efforts made to apply them to that end have resulted in some interesting data regarding the conditions existing in this type of varnish.

TABLE II—EXAMINATION BY PRECIPITATION OF INSOLUBLE POTASSIUM SOAP

SAMPLE No. G.	ADULTERANT		WOOD OIL		ADULTERANT		
	G.	Kind	Soap G.	Cal- cu- lated G.	Re- cov- ered %	Found	
						G.	%
1 3.301	...	...	3.334	3.334	101.0	-0.033	-1.0
1 2.814	0.304	...	2.807	2.807	99.8	0.311	9.9
1 3.012	0.180	Linseed	3.021	3.021	100.3	0.171	5.5
1 2.516	0.506	...	2.508	2.508	99.8	0.514	17.0
1 3.138	...	...	3.170	3.170	101.0	-0.032	-1.0
1 2.859	0.959	Soya	2.874	2.874	100.6	0.944	24.7
1 2.642	0.881	bean	2.645	2.645	100.1	0.878	24.9
1 3.013	...	...	3.006	3.006	99.8	0.007	0.2
1 3.006	0.167	Soya	2.982	2.982	99.2	0.191	6.0
1 2.051	1.302	bean	2.020	2.020	98.1	1.333	39.8
1 2.461	0.125	...	2.536	2.536	103.0	-0.075	-2.9
1 2.791	0.607	Linseed	2.883	2.883	103.3	0.515	15.2
1 2.742	0.380	...	2.761	2.761	100.7	0.361	11.5
1 2.742	0.183	...	2.741	2.741	100.0	0.184	6.3
1 2.528	...	...	2.501	2.501	98.9	0.027	1.1
1 2.524	...	...	2.550	2.550	101.0	-0.026	-1.0
1 2.521	...	...	2.510	2.510	99.5	0.011	0.5
1 2.510	...	...	2.514	2.514	100.2	-0.004	-0.2
1 2.321	0.707	Linseed	2.367	2.367	102.0	0.661	21.8
1 2.428	0.738	...	2.508	2.508	103.3	0.658	20.8
1 3.019	...	...	3.019	3.019	100.0	...	...
1 3.039	0.409	...	3.025	3.025	99.5	0.423	12.3
1 3.199	1.049	Mixed	3.201	3.201	100.3	1.038	24.5
2 3.252	...	...	3.224	3.224	99.1	0.028	0.9
3 3.471	...	...	3.544	3.544	102.1	-0.073	-2.1
4 3.156	...	...	3.014	3.014	95.5	0.142	4.5
4 3.190	...	...	3.092	3.092	96.9	0.098	3.1

NOTE—Wood oils Nos. 1, 2 and 3 were the same as those in Table I. Wood oil No. 4 was furnished by Mr. L. P. Nemzek, representing the Educational Bureau of the Paint Manufacturers' Association. This oil is from American-grown nuts.

An examination of the separated constituents of a Chinese-wood-oil rosin varnish seems to show that the polymerization of wood oil in the presence of rosin is practically as complete as in the oil, subject to the same heat treatment in the absence of rosin. The fatty acid in each case shows a molecular weight double that of the fatty acid of raw wood oil. The difference in characteristics between these two polymerized products has not as yet been satisfactorily accounted for.

A comparison of the molecular weights of the fatty acids from raw wood oil and the light breaks seems to show that this light break is an isomer rather than a polymer, and that there is practically no difference between the light break formed slowly by sunlight alone and that catalyzed by iodine.

UNIVERSITY OF MICHIGAN
ANN ARBOR

OILS OF THE CONIFERAE. II—THE LEAF AND TWIG, AND BARK OILS OF WHITE FIR

By A. W. SCHORGER

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The white fir [*Abies concolor* (Gord.) Parry] is found on the mountain slopes from southern Oregon to Lower California and from Nevada, Utah, and southern Colorado through Arizona and New Mexico. The dense crown consists of short, heavily foliated branches. The leaves at the top of the tree are usually 1 to 1½ inches in length, while those of the lower branches are somewhat longer—1½ to 3 inches.

LEAF AND TWIG OILS

The oils were greenish yellow in color with a green fluorescence with the exception of samples Nos. 2439 and 2487, which were lemon-yellow in color and showed no fluorescence. The residue left after removal of the terpenes by distillation was fluorescent to a marked degree, but this property was not noted in the "green oil" fraction obtained, though the oil owes its green color to this fraction.

The properties of the oils and the yields are given in Table I.

TABLE I—PROPERTIES OF OILS

Sample No.	d_{15}°	n_{D15}°	α_{D25}°	Acid Ester		Ester No. after acetyl.	Ace- tate Per cent	Per cent alcohol		Yield of oil Per cent
				No.	No.			Free	Total	
LEAF AND TWIG OILS										
2176	0.8758	1.4788	—27.94	1.13	12.52	48.88	4.38	10.28	13.73	0.140
2180	0.8738	1.4786	—20.18	1.81	27.34	54.58	9.57	7.65	15.17	0.029
2181	0.8732	1.4786	—21.65	1.43	24.03	52.45	8.41	7.99	14.60	0.050
2183	0.8737	1.4796	—26.87	1.07	20.55	54.22	7.19	9.50	15.15	0.150
2439	0.8720	1.4787	—26.59	1.01	14.48	51.83	5.07	10.57	14.55	0.163
2440	0.8745	1.4790	—24.08	1.32	14.80	47.84	5.18	9.32	13.39	0.095
2487	0.8777	1.4781	—20.11	1.06	18.79	55.51	6.58	10.39	15.56	0.272
						Mean,	6.63	9.39	14.59	0.128
BARK OILS										
			α_{D20}°							
2209	0.8767	1.4833	—20.95	1.22	6.88	23.34	2.41	4.58	6.48	0.07
2423	0.8702	1.4809	—20.15	0.87	6.43	20.45	2.25	3.90	5.67	0.12
						Mean,	2.33	4.24	6.08	0.095

There is a considerable variation in the ester and free alcohol content in the various samples but the total alcohol content is fairly uniform. Samples Nos. 2439 and 2440 were distilled from material taken from the top and base, respectively, of the same tree. The needles from the top of the tree show a slightly greater total alcohol content.

Six hundred grams of oil distilled as follows: 161–165°, 15.5 per cent; 165–170°, 42 per cent; 170–180°, 18.5 per cent; 180–195°, 3 per cent; 195–240°, 13 per cent; 240–310°, 3 per cent.

IDENTIFICATION OF CONSTITUENTS

FURFURAL—The first fraction was shaken out with water. On treating the aqueous extract with aniline and hydrochloric acid a deep crimson color characteristic of furfural was obtained.

α -PINENE—The fraction examined for α -pinene had

the following properties: B. p. 156.5°–159.0°, d_{15}° 0.8671, α_{D22}° –24.29°. The nitrosochloride separated very slowly from the mother liquor. The purified compound melted at 103° and its nitrolpiperidine at 118.5°. The total fractions boiling below 160° amounted to 75 g. (12.5 per cent).

CAMPHENE—The camphene fraction b. p. 160–164° amounted to 8 per cent. The fraction b. p. 160–162°, d_{15}° 0.8695, α_{D23}° –27.39°, was tested according to the method of Betram and Walbaum.¹ On treating the saponified product with water the isoborneol separated as a viscous oil. On steam distillation oil first passed over, followed by isoborneol that solidified in the condenser. The purified isoborneol melted at 209–210° in a sealed tube. The fraction b. p. 162–164° yielded smaller amounts of isoborneol.

β -PINENE—This terpene is the major constituent of the leaf oil, since 254 g. (42.3 per cent) were finally obtained boiling between 164–170°. On oxidation of a fraction, b. p. 164–166.5°, d_{15}° 0.8715, α_{D23}° –23.66°, with alkaline potassium permanganate, large quantities of sodium nopinate were obtained. The free nopinic acid melted at 126.6–127°.

PHELLANDRENE—The fractions b. p. 170–180°, weighing 90 g., gave large amounts of phellandrene nitrite. The fraction b. p. 174–177°, d_{15}° 0.8572, α_{D22}° –28.74°, formed a solid mass of crystals on treatment with KNO₃ and acetic acid. The nitrite melted at 102°. Limonene was not detected as either the dihydrochloride or tetrabromide.

BORNEOL—The oil obtained by saponification of the fraction b. p. 200–240° distilled in about equal proportions between 205–215° and 215–220°. The first portion had the rotation α_{D24}° –29.16°. Both fractions were treated with phthalic anhydride. Saponification of the phthalic esters yielded oils. On oxidizing the latter with chromic acid mixture camphor was obtained melting at 171–172°. Considerably larger yields of camphor were obtained by oxidizing the borneol fraction directly with saturated potassium permanganate solution without attempting its purification through the phthalic ester. The camphor was converted to its semicarbazone melting at 236–237°.

ACETIC ACID—The acids recovered from the ester saponification liquors were precipitated as their silver salts in five fractions. Analysis of portions of the various precipitates without further purification gave a silver content of 63.04–63.72 per cent, showing that acetic acid must be practically the only acid present, since silver propionate theoretically requires 59.91 per cent Ag, silver acetate 64.64 per cent Ag, and silver formate 70.59 per cent Ag. The combined precipitates were recrystallized from water several times. The fine needles obtained were analyzed as follows:

0.1140 g. silver salt gave 0.0736 g. Ag = 64.56 per cent Ag.

"GREEN OIL"—The residue remaining after removal of the ester fraction had a strong green fluorescence. The fraction b. p. 240–310° on redistillation distilled mainly between 265–285°. It had $d_{19.5}^{\circ}$ 0.925, n_{D15}° 1.4936, α_{D20}° –0.49°, for a 37.83 per cent solution

in ether. The oil was emerald-green in color and showed no fluorescence. No solid derivatives were obtained. This oil appears to be similar to the "green oil" obtained by the author from the leaf oil of Douglas fir¹ and showed the same color reactions.

BARK OIL

The bark distilled was about one-quarter of an inch thick and had been peeled from small trees cut for poles. The properties of the oils and the yields are given in Table I.

The following results were obtained on distillation of 110 g. of oil: b. p. 162.5–170°, 65 per cent; b. p. 170–180°, 14 per cent; b. p. 180–192°, 8 per cent; 192–250°, 4 per cent; 250–300°, 5 per cent.

IDENTIFICATION OF CONSTITUENTS

FURFURAL—This aldehyde was detected in the first fraction by the color method. From the intensity of color produced a larger quantity of furfural is present in the bark oil than in the leaf and twig oil.

α -PINENE—By repeated fractionation 10 g. (9.1 per cent) of oil were obtained of b. p. 160–163°, α_{D20}° –16.43°. This oil yielded 2.1 g. (21 per cent) of pinene nitrosochloride. Its nitrolpiperidine melted at 118°.

β -PINENE—The β -pinene fractions distilled as follows: (1) b. p. 163–165°, 14.9 g.; (2) b. p. 165–170°, 51.2 g. The latter fraction had d_{15}° 0.8654, α_{D20}° –22.52°. On oxidation of the oil a yield of 21.7 per cent of sodium nopinate was obtained. The free nopinic acid melted at 126–127°. Five grams of sodium nopinate yielded 24 per cent of nopinone, whose semicarbazone melted at 188°.

DIPENTENE—The oil boiling between 170–180° had the rotation α_{D21}° –29.37°. On treating the dry oil with dry HCl gas a dihydrochloride m. p. 49–50° was obtained, but no solid derivative was obtained on bromination.

ALCOHOL FRACTION—The amount of oil obtained by saponification of the fraction b. p. 192–250° was too small for identification of the alcohol present. The ester and free alcohol have been calculated as bornyl acetate and borneol as it is most probable that these are the constituents present.

"GREEN OIL"—The fraction b. p. 250–300°, weighing 5.4 g., was bright green in color and from its color reactions appeared identical with the "green oil" from the leaf and twig oil. It is possible that the "green oil" in the leaf and twig oil is not derived from the needles themselves, but from the bark of the twigs.

SUMMARY

The oils of white fir have approximately the following composition:

Percentages	Leaf and Twig oil	Bark oil
Furfural	Trace	Trace
<i>l</i> - α -Pinene.....	12	9
<i>l</i> -Camphene.....	8	
<i>l</i> - β -Pinene.....	42	60
<i>l</i> -Phellandrene.....	15	12–13
Ester as bornyl acetate	6.5	2.5
Free borneol.....	9.5	4.5
"Green oil".....	3	5
Losses.....	4	7

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¹ Jour. für prakt. Chem., [2] 49 (1894), 1.

¹ Jour. Am. Chem. Soc., 35 (1913), 1895–7.