

oil turned into a yellow solid which was freed of the mother liquor by decantation. This solid was contaminated by bismuth sulfide so that it was recrystallized from hot water. The yellow crystals obtained were very slightly soluble in cold water, soluble in hot water and glycerin.

Calculated for  $\text{Bi}(\text{SCH}_2\text{CO}_2\text{NH}_2)_3$ : Bi—43.6%; S—20.1%; N—8.7%.  
Found: Bi—45.6%; S—20.58%; N—8.0%.

The biological tests on these compounds were carried out in the Biological Laboratories of E. R. Squibb and Sons, New Brunswick, N. J.

- (1) Harden and Dunning, *J. Am. Chem. Soc.*, 49 (1927), 1017.
- (2) Abel and Rowntree, *J. Pharmacol. & Exper. Therap.*, 2 (1910), 11.

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### PHYTOCHEMICAL NOTES.\*

#### NO. 108. THE NON-HEPTANE CONSTITUENTS OF JEFFREY PINE OIL.

BY C. W. SONDERN.

Early in 1927 an understanding was reached with Dr. Graham Edgar of the Ethyl Gasoline Corporation of Yonkers, N. Y., in accordance with which a large amount of Jeffrey pine oil was to be sent to the Wisconsin Pharmaceutical Experiment Station for rectification of its principal constituent, the heptane. The non-heptane constituents were to be used for further investigation of these substances, whereas the heptane fraction was to be forwarded to Yonkers for the study of the standardization of gasoline as fuel in internal combustion engines. The Jeffrey pine oil was produced in California during the summer of 1927 as a coöperative enterprise between the Ethyl Gasoline Corporation, the local representative of the Bureau of Forestry, and a third party, the Chemical Corporation of California. The material, four drums in all, was received at Madison, in the fall of the same year.

The materials obtained in the separation of the heptane fraction from the Jeffrey pine oil may, for the sake of convenience, be grouped in the following manner:

- I. The aqueous cohobate.
- II. Oily fractions distilling below the b. p. of *n*-heptane ("Vorlauf").
- III. The heptane fractions forwarded to the Ethyl Gasoline Corporation.
- IV. Oily fractions distilling above the b. p. of *n*-heptane after removal of the aldehydes by shaking them with hot conc.  $\text{NaHSO}_3$  solution.
- V. The oily aldehydes regenerated from the sodium acid sulphite addition products.<sup>1</sup>
- VI. Some resinous materials from drums and still which were discarded.

*I. Examination of the Aqueous Cohobate.*—The aqueous distillates collected in connection with the various fractionations in the first distillation of the Jeffrey pine oil were combined and concentrated. The original volume of nine gallons was distilled and the first third retained. This fraction was neutralized with barium carbonate and evaporated to three liters in a large still. The filtrate was further concentrated in an evaporating dish to one hundred cc. when the concentrate was

\* From the Laboratory of Edward Kremers.

<sup>1</sup> P. A. Foote, *Jour. A. Ph. A.*, 18 (1929), 350.

placed in a vacuum desiccator over KOH until dry. The resulting residue was washed from the dish with 1 p. c. nitric acid and filtered. The filtrate was treated with silver nitrate. The precipitated silver salt having been washed and dried was heated and the residual silver weighed. 0.1923 Gm. of silver salt, dried at 110°, yielded 0.1128 Gm. of metallic silver.

The silver content as computed for the following silver salts is:

		Found.
For Ag acetate	65.18 p. c.	
For Ag propionate	59.64 p. c.	58.60
For Ag butyrate	55.36 p. c.	

## II. Examination of the Constituents Boiling Below the B. P. of *n*-Heptane.—

From the Report on the Rectification of Crude Jeffrey Pine Oil,<sup>1</sup> it becomes apparent that the "Vorlauf" of the four drums was collected separately and in somewhat different amounts. Whereas for the purpose of the report referred to approximations were deemed sufficient, the more accurate amounts are herewith recorded, also the density of each.

	Amount.	$d_{25.5}^{\circ}$
Vorlauf from drum I	700 cc.	0.6846 <sup>1</sup>
Vorlauf from drum II	750 cc.	0.6770
Vorlauf from drum III	750 cc.	0.6770
Vorlauf from drum IV	3800 cc.	0.6780
<hr/> Total	<hr/> 6000 cc.	

<sup>1</sup> The higher density is due to drippings from the condenser left from higher fractions previously distilled.

For the sake of convenience I and II were mixed for fractionation, also III and IV.

*Fractionation of III and IV.*—In order to neutralize any acid that might be present 10 Gm. of sodium carbonate were added to the mixed portions and the mixture fractionated with the following results:

No.	B. P.	Vol.	$d_{25.5}^{\circ}$
1	-85°	60 cc.	0.6735
2	85-90°	178 cc.	0.6790
3	90-92°	307 cc.	0.6780
4	92-95°	950 cc.	0.6770
5	95-96°	1000 cc.	0.6780
6	96-97°	1000 cc.	0.6785
7	97-98°	125 cc.	0.6789

Lots I and II were then introduced into the still and the fractionation continued with the following results:

No.	B. P.	Vol.	$d_{25.5}^{\circ}$
8	-75°	200 cc.	0.6919 <sup>1</sup>
9	75-80°	99 cc.	0.6890
10	80-86°	104 cc.	0.6835
11	86-90°	178 cc.	0.6800
12	90-92.5°	185 cc.	0.6790
13	92.5-94.5°	425 cc.	0.6778
14	94.5-95.5°	425 cc.	0.6785
15	95.5-97°	468 cc.	0.6789
16	97-98°	266 cc.	0.6790

It becomes apparent that these fractions consist in large part of *n*-heptane (b. p. 98.4°) as was to be expected. However, the lower boiling points of practically all of the fractions suggest the presence of other substances. In order to isolate these, another fractionation was resorted to. Although the fractions recorded above do not agree, it is easy enough to select corresponding fractions to be mixed for the next fractionation. Thus Fractions 8 and 9 were mixed and distilled into five fractions. At this point the distillation was stopped and Fraction 10 was added, and three more fractions were collected before the Fractions 1, 2 and 11 were added. In this manner nine fractions (1-6, 9, 10, 11) distilling below 85° were obtained.

Inasmuch as some of the thirteen fractions of the next table were found to contain appreciable amounts of water-soluble material, this was removed by shaking the oil with small amounts of water in a stoppered graduated cylinder until the volume was no longer appreciably reduced. The densities of the oily fractions before and after shaking with water are recorded, also the percentage of water-soluble constituents.

No.	Distillation Range.	$d_{25}$		Percentage of Water-Soluble Constituents.
		I Before Washing.	II Washed.	
Fractions 8 and 9 (b. p. 75° and --75-80°) yielded on fractionation:				
1	-57°	0.7275	0.6735	46.7 p. c.
2	57-57.5°	0.7365	0.6745	46.4 p. c.
3	57.5-58.5°	0.7355	0.6750	48.6 p. c.
4	58.5-70°	0.7268	0.6780	40.0 p. c.
5	70-85°	0.6880	0.6780	8.8 p. c.
At this point Fraction 10 was added. (B. p. 80-86°.)				
6	-85°	0.6760	0.6775	18.1 p. c.
7	85-87°	0.6770	0.6755	1.5 p. c.
8	Residue	0.6785	Same	..
Now the still was refilled with Fractions 1, 2 and 11. (B. p. 85°, -85-90° and 86-90°.)				
9	-65°	0.7760	0.6750	33.7 p. c.
10	65-70°	0.6915	0.6735	27.3 p. c.
11	70-85°	0.6840	0.6750	6.5 p. c.
12	85-90°	0.6775	0.6755	1.9 p. c.
13	Residue	0.6775	....	..

The aqueous solution of the water-soluble constituents was deprived of much of its water by means of anhydrous copper sulphate and the volatile organic substances were distilled over on a sand-bath at a temperature below 98°. About 100 cc. of distillate were thus obtained. This distillate was further dehydrated with anhydrous copper sulphate and fractionated. The fractions and their densities are herewith recorded:

Fraction.	B. P.	$d_{20}^*$
1	55-60°	0.7960
2	60-61°	0.8004
3	61-65°	0.8050
4	65-70°	0.8056
5	70-75°	0.8171

*Identification of Acetone.*—This ketone boils at 56.3° and has a density of 0.7900 at 25°. Its presence in Fraction 1 was established by

1. By the iodoform test.
2. As dibenzylidene acetone, which was obtained in yellow crystals melting at 108°, when recrystallized at 109°. The recorded m. p. is 111-112°.
3. By sodium nitroprusside test which yielded the characteristic violet color reaction.

*Identification of Methyl Alcohol.*—This alcohol boils at 64.7° and has a density of 0.7980 at 15°. Its presence in Fractions 3 and 4 could not be established.

The following tests were applied:

1. The methyl salicylate test was not successful because any odor thereof was covered by that of other volatile constituents.
2. With 3,5-dinitrobenzoic acid crystals were obtained which melted at 81-82°, and upon recrystallization at 86°. The methyl ester melts at 107.5°. (See ethyl ester.)
3. By oxidation with a hot copper wire and subsequent treatment with resorcinol-sulphuric acid, the test yielded the characteristic red flocks. (Possibly due to formaldehyde present as such.)

*Identification of Ethyl Alcohol.*—With 3,5-dinitrobenzoic acid Fraction 5 yielded crystals which melted at 92-93°. This is the recorded melting point for the ethyl ester.

*Identification of Aldehydes.*—All fractions yielded a positive test with Schiff's reagent. Fraction 3 gave a semicarbazone melting at 125-126°. Isobutyric aldehyde semicarbazone melts at this temperature.

Fraction 1 was tested by means of the resorcinol-sulphuric acid test and produced the characteristic red flocks indicating the presence of formaldehyde.

As was to be expected, only insignificant traces of these water-soluble substances were isolated. From their coefficient of distribution between water and heptane, by far the larger proportions have, no doubt, been discarded with the aqueous distillate in the steam distillation of the volatile oil from the oleoresin. Though of little if any technological significance, it would be worth while biochemically to cohobate the aqueous distillate if the production of Jeffrey pine oil is again undertaken on a large scale.

*Analysis of Water-Insoluble Fractions.*—Fractions 1-6 and 9-11 from which the water-soluble constituents had been removed were combined and fractionated as follows:

No.	B. P.	Vol.	$d_{20}^{\circ}$
1	-85°	22 cc.	0.6713
2	85-90°	20 cc.	0.6721
3	90-95°	42 cc.	0.6752
4	95-97°	86 cc.	0.6784
Residue			

All the fractions failed to give Schiff's test for aldehydes.

Ten-cc. portions of the oily Fractions 1 and 3 were acetylated, washed with NaCl solution until free of acid and dried over anhydrous sodium sulphate. Two samples of each fraction of acetylated oil were saponified with standard alcoholic potassium hydroxide. The resulting saponification number was zero, thus indicating the absence of alcohols and esters. It, therefore, appears that the residual oil consists entirely of hydrocarbons, chiefly *n*-heptane.