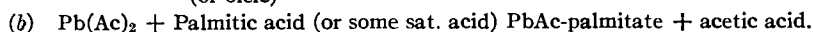
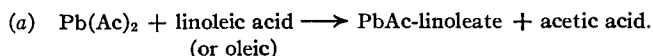


No.	B. P., ° C.	Iodine Value.	Mol. Wt. from Acid Values.		Saponification Value.	
1	-186 (8 mm.)					
2	186-188 (7 mm.)	110.7	290.0		193.4	
		110.3	291.3	290.7	192.1	192.8
3	186-188 (7 mm.)					
4	188-190 (7 mm.)					
5	190	120.5	290.7		193.0	
			291.8	291.3	192.3	192.6
6	190 + residue					

The very small change in boiling point would seem to indicate a very constant boiling constituent. However, the very high iodine value in these esters is noteworthy. The iodine value of oleic acid is 90.0 and that of methyl oleate about 86.0. This would indicate that a great deal of the linoleic acid had not been removed as tetra bromide. This fact was established by isolating tetrabromstearic acid when the freed acid was brominated in petroleum ether solution.

- (1) This percentage is obtained from fat extracted from the main experiment.
- (2) Computed with reference to the seed coat.
- (3) Computed with referenced to the entire seed.
- (4) Computed with reference to the endosperm.
- (5) Computed with reference to the entire seed.
- (6) The method of Zeleny and Baily, *J. I. E. C.*, 24, 109 (1932), was used.
- (7) Hilditch and Vidyarthi, *Royal Society, A.* 122, 552 (1929).
- (8) Hilditch, *Fat and Waxes*, 74 (1927); Twitchell, E., *J. I. E. C.*, 13, 806 (1921).
- (9) Consideration of this fact, that at 6° a great deal of oleic and linoleic acids, in a ratio approximating that in the original, comes down while at 18° very little separates should be worth recalling when this experiment is repeated. If an alcoholic solution of lead acetate is added to an alcoholic solution of fatty acids the following situation arises:



In this particular case reaction "a" predominates and the opportunity of PbAc-palmitate to react with another palmitic acid molecule to yield $\text{Pb}(\text{palmitate})_2$ is remote compared with its opportunity to react with a molecule of linoleic acid to yield Pb palmitate-linoleate, which undoubtedly is more soluble than $\text{Pb}(\text{palmitate})_2$ but less soluble than $\text{Pb}(\text{linoleate})_2$. The precipitate at 6° was probably a half-saturated and half-unsaturated lead soap such as Pb palmitate-linoleate. At a higher temperature only the saturated lead soaps settle out.

(10) *J. I. E. C.*, 6, 564 (1914).

(11) Rosenthaler-Ghosh, "The Chemical Investigation of Plants," 83 (1930).

THE LEAF OILS OF WASHINGTON CONIFERS: VII. JUNIPERUS OCCIDENTALIS.*

BY E. V. LYNN AND LOUIS FISCHER.¹

Juniperus occidentalis Hook. is a tree 20 to 40 feet or more in height. It grows on mountain slopes and high prairies of western Idaho, eastern Washington and Oregon and in the Cascade and Sierra Nevada mountains. Seldom is it found at elevations less than 6000 feet.

The leaves and branches for this work were collected in 1930 near Bend, Oregon. From 600 pounds of fresh material was obtained 986 Gm. of oil by steam dis-

* Scientific Section, A. PH. A., Washington meeting, 1934.

¹ Seattle, Washington, June 7, 1934.

tillation, a yield of about 0.36 per cent. Due to various reasons the oil was not examined at the time. Three years later it had resinified somewhat and was, therefore, rectified with steam, giving a light yellow product with a characteristic odor of Juniper.

The constants, determined in the usual way, were: d_{25}^4 0.9212; n_D^{25} 1.4745; $[\alpha]_D^{25}$ +21.91°; acid number 1.45; saponification number 110.53 (38.17 per cent of bornyl acetate); after acetylation 149.58 (11.06 per cent of free borneol, 41.05 per cent of total borneol). Aldehydes and ketones and primary alcohols were absent or present in very small quantities.

Free Acids.—Extraction by 5 per cent sodium carbonate gave a small amount of free acids in which acetic acid was identified by color reactions and by conversion to ethyl acetate. Judging by odor, there may also be present a small amount of acid resembling valeric.

Phenols.—Extraction by 5% NaOH solution gave 0.5 per cent of a dark brown liquid with an odor of creosote, which did not solidify above -15° C. No nitroso compound or urethane could be obtained from it, but it gave color reactions similar to carvacrol. With ferric chloride in aqueous solution it produced a violet color and in alcoholic solution a yellow-brown with a green tinge. The Flückiger test with chloroform and alkali resulted in a light red color, somewhat darker than with carvacrol.

The remaining oil was fractionated at 10 mm. and that portion boiling below 95° C. was repeatedly refractionated.

Fraction.	Per Cent.	Refraction.
155-160°	1.61	
160-162	1.69	1.4700
162-169	10.15	1.4736
169-175	12.30	1.4805
175-180	6.31	1.4845
180-185	2.31	1.4802
Total	34.37	

Camphene.—The first fraction $[\alpha]_D +9.9^\circ$, gave no nitrosochloride and probably contained no pinene. Portions of each of the first two fractions were hydrated by the well-known Bertram-Walbaum method, giving light yellow oils. No phenylurethanes could be obtained, but the odor was decidedly that of isborneol and a camphoraceous odor was noted after oxidation with chromic acid. The amount of oil was too small to permit exact identification, but the presence of some camphene is indicated.

The third fraction was oxidized with potassium permanganate in the usual way for betapinene but no product like sodium nopinate or nopinone could be obtained. This fraction also gave no hydrochloride.

Alpha Phellandrene.—Fractions three, four and five gave copious yields of a nitrite melting at 112° C. This was repeatedly dissolved in chloroform and precipitated with methyl alcohol, finally giving a melting point of 114° C. This shows the presence of alpha phellandrene.

Fraction five had an odor of limonene but gave no nitrosochloride and no bromide, nor did fraction four.

Cymene.—The last two fractions contained small amounts of cymene, as was

shown by oxidation with hot potassium permanganate to *p*-hydroxy isopropyl benzoic acid, melting at 154–155° C.

The oil of higher boiling point was saponified by 3 per cent alcoholic potassium hydroxide for two hours and then submitted to repeated fractionation at 10 mm. into three portions.

Fraction.	Per Cent.	Refraction.
...- 95°	1.07	1.4778
95-120	39.69	1.4744
120-125	1.84	1.4885
Above 125 and loss	23.03
Total	65.63	

Borneol.—The first two consisted almost entirely of borneol which was separated in the crystalline state, melting point 203–204° C., phenylurethane 138° C. Oxidation of the oil gave camphor, identified by odor and by the semicarbazone melting at 235–236° C.

Although terpineol was suspected, no nitrosochloride could be obtained from the second fraction. Also cadinene was not present in the last distillate nor in the residue, since no hydrochloride could be obtained.

Combined Acids.—The alkaline liquor from saponification was concentrated, acidified and then distilled with steam. Practically all of the acid was found in the distillate and appeared to consist almost entirely of acetic acid. This was identified as before by conversion to ethyl acetate.

Summary.—The fresh leaves and branches gave 0.36 per cent of oil whose composition was found to be about: bornyl acetate 40; borneol 11; alpha phellandrene, cymene and probably camphene 35; acetic acid 0.2; phenols 0.5; compounds of higher boiling point and loss 14 per cent.

DRUG EXTRACTION. IV. THE EFFECT OF VARIATION IN SOLVENTS ON THE EXTRACTION OF JALAP.^{1,2}

BY WILLIAM J. HUSA³ AND PAUL FEHDER.

Jalap having been selected as a typical resin-containing drug, a study was made of the effect of solvents in relation to swelling, penetration, imbibition and extraction.

EXPERIMENTAL PART.

Material Used.—From a reputable dealer, a 125-lb. shipment of Jalap U. S. P. was obtained, consisting of 10 lbs. whole drug, 40 lbs. of 60 mesh and 25 lbs. each of 20, 40 and 80 mesh, according to the following specifications: "The above samples are to be prepared by taking 125 lbs. of jalap, selecting a representative sample of 10 lbs. for the whole root and a representative 40-lb. sample to be milled to 60 mesh, and three separate 25-lb. samples to be milled to 20, 40 and 80 mesh, respectively. Each portion is to be milled separately so that all portions will be as nearly alike as possible, except for the difference in milling."

¹ Presented before the Scientific Section, A. Ph. A., Washington, D. C., 1934.

² This paper is based on a thesis presented to the Graduate Council of the University of Florida by Paul Fehder, in partial fulfilment of the requirements for the degree of Master of Science in Pharmacy.

³ Head Professor of Pharmacy, University of Florida.