

cooled the pitch under slight pressure, to avoid the formation of voids. The slow cooling always caused a marked increase in apparent specific gravity with the harder pitches, while with soft pitches the difference is negligible.

The writer hopes that this paper on the homely subject of specific gravity will be useful in some measure to workers in general, and can state that, in his experience, the methods recommended here are rapid, convenient, and sufficiently accurate.

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OILS OF THE CONIFERAE: IV. THE LEAF AND TWIG OILS OF DIGGER PINE, LODGEPOLE PINE, AND RED FIR

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Received November 2, 1914

It is well known at the present time that the oleoresins of the digger pine (*Pinus sabiniana*) and Jeffrey pine (*Pinus jeffreyi*) yield oils consisting almost entirely of *n*-heptane. Examination of the leaf and twig oil of the digger pine has revealed the very interesting fact that heptane was present in the sample to the extent of only about 3 per cent, the remainder of the oil consisting of aromatic bodies which are principally terpenes. It may be assumed with safety that this small percentage of heptane was derived from the small twigs during distillation, since the latter were not separated from the leaves. The phytochemical processes taking place in the leaves and in the woody portions of the tree are, accordingly, entirely different, since the oil from the former consists of aromatic compounds and the oil from the latter of aliphatic derivatives.

Anisic acid was obtained by oxidation of certain fractions of the oils from digger and lodgepole pines. Lack of material prevented obtaining conclusive evidence as to the parent substance from which the anisic acid was derived, and for the same reason the presence of borneol and certain terpenes can not be shown with absolute certainty. The data obtained, however, should be of important assistance to the chemist who is fortunate enough to obtain material for further investigation.

LEAF AND TWIG OIL OF DIGGER PINE (*Pinus sabiniana*, DOUGL.)

The physical and chemical constants of the oils are given in Table I.

The sample of 238 grams gave the following fractions: 100°–152°, 6.0 per cent; 152°–160°, 10.0 per cent; 160°–170°, 52.0 per cent; 170°–188°, 15.0 per cent; 188°–235°, 8.5 per cent; 235°–290°, 2.3 per cent; residue, 6.0 per cent.

HEPTANE—The lower boiling portions of the oil were fractionally distilled and repeatedly treated with concentrated sulfuric acid. By this treatment 7.2 grams (3.0 per cent) of oil were finally obtained, having the specific gravity 0.7013 at 15° and boiling between 98.5° and 101°. Pure *n*-heptane boils at 98.4° and has a specific gravity at 15° of 0.6880.

α-PINENE—The fraction boiling at 156–157° had d_{15}^0 0.8618 and α_{D20}^0 –26.24°. A good yield of pinene nitrosochloride was obtained. The nitrosochloride was thoroughly washed with methyl alcohol and dissolved in a small amount of hot chloroform. The crop

TABLE I—THE PHYSICAL AND CHEMICAL CONSTANTS OF THE LEAF AND TWIG OILS

Sample	Sp. gr. 15°	Ref. Ind. 15°	Optical rotation α_{D20}^0	Acid No.	Ester No.	Ester No. after acetyla- tion	Per cent yield of oil
DIGGER PINE:							
2493	0.8566	1.4670	–20.93°	2.05	11.98	37.16	0.102
2494	0.8543	1.4708	–38.36°	1.91	9.48	29.84	0.085
2496	0.8517	1.4671	–30.75°	1.47	6.77	25.86	0.078
LODGEPOLE PINE:							
2495	0.8690	1.4831	–17.84°	0.90	6.02	32.30	0.234
RED FIR:							
2529	0.8665	1.4861	–16.70°	0.75	9.93	36.22	0.154

of crystals obtained on cooling, after washing with alcohol, melted at 104–105°. From the chloroform mother liquor a further amount of crystals was obtained on addition of methyl alcohol. These crystals after washing with methyl alcohol melted at 105°. The nitropiperidine derivative melted at 117°. The total α -pinene fractions amounted to 58 to 59 per cent.

The relatively small amount of oil boiling between 160–170° was examined for β -pinene with negative results.

LIMONENE—The total limonene fractions amounted to about 24 per cent. The fraction boiling at 170–175° and having α_{D21}^0 –40.79° gave negative results for phellandrene. Sylvestrene was apparently absent since the dihydrochloride obtained melted at 49–50°. The fraction boiling at 175–177° yielded a tetrabromide melting at 104°, the melting point of limonene tetrabromide.

ESTER FRACTION—The portion boiling at 206–235° was saponified and distilled with steam. The recovered oil was then oxidized with a saturated solution of potassium permanganate and again distilled with steam. Only a few drops of oil having the odor of camphor were obtained. On acidifying the oxidation liquor an acid was obtained that crystallized from hot water in thin needles and sublimed readily, giving crystals melting at 183–184°. A portion of the acid weighing 0.1637 g. required 10.62 cc. of *N*/10 NaOH for neutralization, giving a neutralization equivalent of 154.2. The properties of the acid showed it to be anisic acid, $C_6H_4 \begin{matrix} \text{OCH}_3 \\ \text{COOH} \end{matrix}$, the latter melting at 183–184° and having a neutralization equivalent of 152.

The boiling point of the fraction, and other considerations, render it probable that the anisic acid was derived from methylchavicol, the latter boiling at 215–216°. Lack of material, however, prevented obtaining conclusive evidence on this point. Methylchavicol has never been previously detected in the needle oils of the coniferae but was found by Schimmel and Company¹ in "pine oil."

"GREEN OIL"—Only a few drops of oil distilled between 235 and 265°. Between 265 and 290°, 5.4 grams (2.3 per cent) of a light green oil were obtained. When a drop of the oil was dissolved in glacial acetic acid

¹ Report for April, 1910.

and a drop of concentrated sulfuric acid was added the solution turned saffron, then crimson.

LEAF AND TWIG OIL OF LODGEPOLE PINE
(*Pinus contorta*, LOUD.)

The physical and chemical constants of the lodgepole pine oil are given in Table I.

The sample examined amounted to 414 g. and gave the following results on distillation: 164°–170°, 40 per cent; 170–175°, 27 per cent; 175–183, 10.5 per cent; 183–205°, 5.5 per cent; 205–235°, 7 per cent; 235–255°, 0.5 per cent; 255–284°, 6.5 per cent.

FURFURAL—A qualitative test for furfural was obtained in the aqueous extract of the first fraction by means of aniline and hydrochloric acid.

α -PINENE—After repeated fractionation, 12.6 g. (3 per cent) of oil were obtained, having the following properties: b. p. 156–160°, d_{15}° 0.8662, α_{D25}° –24.85°. α -Pinene was identified by means of the nitrosochloride melting at 103.0–103.5° and the nitrolpiperidine melting at 118°.

CAMPHENE—The fraction distilling at 160–164° and having d_{15}° 0.8692, α_{D25}° –23.77°, weighed 22.7 g. (5.5 per cent). This oil was treated with glacial acetic acid-sulfuric acid mixture. On distilling the saponified oil with steam, the greater portion of the distillate came over as an oil. The small amount of solid isoborneol that formed in the condenser melted at 205–207° after one crystallization from petroleum ether.

β -PINENE—The greater portion of the original oil consisted of β -pinene, 205.5 g. (49.6 per cent) being collected between 164–170°. One hundred grams of oil boiling at 166–168° and having d_{15}° 0.8680, α_{D24}° –21.16°, were oxidized with alkaline potassium permanganate. The crystalline sodium nopinate obtained yielded on acidification nopinic acid melting at 127°.

PHELLANDRENE—This terpene was found to be present in considerable amounts in the fractions boiling between 170–180°. The fraction boiling at 170–173° and having α_{D25}° –19.94° gave the largest yield of phellandrene nitrite, the latter melting at 102°.

DIPENTENE—Apparently, owing to the presence of considerable phellandrene, it was not possible to obtain a crystalline tetrabromide. The following fractions were examined: (1) b. p. 173–175°, d_{15}° 0.8577, α_{D25}° –22.06°, weight 33.6 grams; (2) b. p. 175–180°, d_{15}° 0.8577, α_{D25}° –21.85°, weight 19.8 g. By dissolving a portion of fraction (2) in dry ether and saturating with dry HCl gas it was possible to obtain dipentene dihydrochloride melting at 49°.

ESTER FRACTION—The fraction boiling at 205–235° was saponified with alcoholic potash. The oil recovered by steam distillation, having the rotation α_{D25}° –15.58°, was treated with a saturated solution of potassium permanganate until reduction of the solution ceased. On steam distillation a small amount of oil having a strong camphor odor was obtained, but the quantity was too small for further identification. The oxidation liquor was then filtered hot to remove manganese sludge and after cooling extracted with ether. The ether extract gave a little viscous oil

having a cinnamon odor. The aqueous solution when acidified gave a copious crystalline precipitate that after sublimation melted at 183–184° and was identified as anisic acid. It is very probable that in this case, as well as in that of the needle oil of digger pine above, the anisic acid may be attributed to the presence of methylchavicol.

CADINENE—The fractions boiling between 265 and 284° were rich in cadinene, the oil having the rotation α_{D21}° +14.69°. The crystals obtained on treatment with HCl gas melted at 117–118° and had in ethereal solution the specific rotation $[\alpha]_D$ –45.66° calculated from the following values:

$$\frac{\alpha}{l} = \frac{-1.375^{\circ}}{1} \quad \frac{p}{d} = \frac{4.125}{0.7300}$$

LEAF AND TWIG OIL OF RED FIR (*Abies magnifica*, MURR.)

The oil examined had a light green color and a pungent, unpleasant odor. The physical and chemical constants are given in Table I.

The sample weighing 193 grams distilled as follows: 167–170°, 10 per cent; 170–181°, 47.5 per cent; 181–190°, 12.0 per cent; 190–236°, 9.0 per cent; 236–260°, 13 per cent.

FURFURAL—This aldehyde was qualitatively detected in the first fraction.

α -PINENE—By repeated fractionation 3.6 g. of oil were obtained which boiled at 160–164°. When treated with ethyl nitrite and hydrochloric acid an intense green coloration characteristic of the formation of pinene nitrosochloride developed, but no crystals deposited. There is little doubt that, with sufficient oil for a careful fractionation, the presence of α -pinene could be definitely established.

β -PINENE—The oil boiling at 164–168° had α_{D24}° –25.54°, d_{15}° 0.8620, and yielded sodium nopinate on oxidation. The free nopinic acid melted at 126–127° which proved the presence of β -pinene. From 16–18 per cent of this terpene is present in the oil.

PHELLANDRENE—Phellandrene was the only terpene that could be detected in the fractions boiling above 168° and constitutes about 52 per cent of the original oil. The fraction boiling at 173–177°, d_{15}° 0.8537, α_{D24}° –21.42°, gave a copious precipitate of phellandrene nitrite melting at 102–103°. Dipentene could not be detected as either the dihydrochloride or tetrabromide.

BORNEOL—Saponification of the fraction, boiling point 206–236°, followed by steam distillation yielded an oil. The oil was then oxidized and distilled with steam. The amount of solid camphor that collected in the receiver was too small for further investigation.

“GREEN OIL”—There were obtained between 255° and 260°, 22.3 g. of a deep green oil having the following properties: d_{15}° 0.8963, n_{D15}° 1.4952, specific rotation $[\alpha]_D$ –6.05°. When a drop of the oil was dissolved in glacial acetic acid and treated with bromine vapors the solution first turned purple, then deep blue. No crystalline derivative was obtained.

SUMMARY

The constituents present in the oils examined, with their approximate percentages, are the following:

LEAF AND TWIG OILS OF	Digger Pine	Lodgepole Pine	Red Fir
Constituents Present	Per cent	Per cent	Per cent
Furfural.....	Trace	Trace	Trace
n-Heptane.....	3	3	3
l- α -Pinene.....	58-59	3	?
l-Camphene.....	...	5-6	...
l- β -Pinene.....	...	49-50	16-18
l-Phellandrene.....	...	19	52
Dipentene.....	0
l-Limonene.....	18
Bornyl ester (as acetate).....	3.5	2	3.5
Free alcohol (as l-borneol).....	6	7.5	7.5
Methylchavicol.....	?	?	...
"Green oil".....	2-3	?	13
Cadinene.....	...	6	6
Losses by polymerization, etc.....	9.5	6	6

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THE ELECTROLYTIC SEPARATION OF ZINC, COPPER AND IRON FROM ARSENIC

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Received November 4, 1914

Satisfactory electrolytic methods for the quantitative separation of zinc and iron from arsenic have not been developed up to this time. With respect to the separation of copper from arsenic, several methods are in use, namely, in acid solution according to Freudenberg,¹ and in ammoniacal and cyanide solutions as first suggested by Smith and Frankel,² and McCay.³

The idea of separating arsenic from other metals by using an electrolyte of sodium or potassium hydroxide, although by no means novel, has not previously been developed to a workable basis except in the separation of tin and arsenic by Lampen,⁴ whose work seems to have been overlooked by more recent writers. A Fischer⁵ says relative to separating zinc from arsenic that it has never been investigated and is only conceivable in an alkaline zincate solution with a definite voltage.

The precipitate formed on adding potassium or sodium hydroxide to the solution of a heavy metal is in the case of some metals soluble in an excess of the precipitant, forming a strongly alkaline solution from which the metal can be deposited by the electric current. Zinc and lead are examples of this, while arsenic, on the other hand, exists in solution as an alkaline arsenate or arsenite, and therefore travels toward the anode. With many metals, such as iron and copper, the precipitate is not dissolved by an excess of caustic alkali, but its formation may often be prevented by the action of certain organic substances, particularly citric and tartaric acids, and from these solutions the metal is easily deposited. Alkaline electrolytes are capable, therefore, of rather wide application.

In this paper we wish to describe the conditions which were found to give excellent results in the separation of arsenic from copper, from iron, and more especially from zinc. Some work is being done upon other metals, notably lead, but this is not yet ready for publication.

In all of these separations the arsenic must exist

in the higher state of oxidation, otherwise a small quantity will be found in the cathode deposit, and some may also be volatilized.

ZINC FROM ARSENIC

It is necessary in connection with our official work in this laboratory to examine numerous samples of zinc arsenite and products containing it. It was in the course of investigations conducted on methods for analyzing these substances that the following experiments were undertaken.

The deposition of zinc from a caustic electrolyte in the absence of arsenic has been so fully discussed by others that we shall not take it up here except to say that we have found it entirely satisfactory.

Since a platinum electrode is injured by the deposition of zinc, the cathode used was a nickel dish, preferably with a surface which has been roughened either by etching or sand blasting. The experiments recorded here were very satisfactorily carried out in ordinary nickel crucibles of about 125 cc. capacity, offering to the deposit about 90 cm². of surface. The anode consisted of a No. 14 (B. & S.) platinum wire bent in the shape of a flat oval-shaped paddle, whose blade is about 2.5 X 2.0 cm., and suspended from the spindle of the rotating mechanism so that the paddle blade is just completely immersed in the liquid. This form of apparatus, besides being readily obtainable, has the advantage of permitting an unusually rapid agitation of the electrolyte.

PREPARATION OF SOLUTIONS—For the zinc solution a weighed amount of very pure zinc oxide¹ was dissolved in dilute sulfuric acid and made to a definite volume.

For the arsenic a solution of pure arsenic acid was used, which was standardized by the iodometric method described later.

Measured amounts of the zinc and arsenic solutions were mixed and sodium hydroxide or potassium hydroxide (50 per cent solution) added until the solution became clear, and then in excess to the extent of about 20 g. The solution was diluted to about 95 cc. and electrolyzed. The electrolysis was thus started at room temperature, but the liquid quickly became heated nearly to boiling.

It was found, as mentioned by Amberg,² that by using potassium hydroxide decidedly better zinc deposits were obtained than with sodium hydroxide. When sodium hydroxide was used, the deposit frequently showed a tendency to be spongy, although this could be remedied somewhat by increasing the rate of anode rotation. The presence of many organic substances in small quantities will also greatly increase the adherence of the deposit.³ We found that glycerol and a mixture of equal parts of glycerol and alcohol worked very well in these experiments. Even alcohol alone had the same effect, but in this case a reddish brown resinous body was formed during the electrolysis. This did not vitiate the results, but rendered the siphonate more difficult to handle.

¹ The zinc oxide was analyzed by several methods with the greatest care and found to contain 99.84 per cent ZnO and 0.14 per cent moisture.

² *Ber.*, 36 (1903), 2489.

³ Cf. Gmelin-Kraut, "Handbuch der anorg. Chemie," 4 (1), s. 559 et seq. (1911).

¹ *Z. physik. Chem.*, 12 (1893), 117.

² *Amer. Chem. Jour.*, 12 (1890), 428.

³ *Chem. Ztg.*, 14 (1890), 509.

⁴ *Chemische Industrie*, 1907, 128.

⁵ *Electroanalytische Schnellmethoden*, 1908, 246.