[CONTRIBUTION FROM THE INDUSTRIAL-FARM PRODUCTS DIVISION, BUREAU OF CHEMISTRY AND SOILS]

Composition of the Non-Phenol Portion of Bay Oil[1]

BY S. PALKIN AND P. A. WELLS

The major part of the oil of bay[2] (obtained from the leaves of *Pimenta acris*, or *Bois d' Inde*) consists of phenols, principally eugenol with some chavicol.

The non-phenol portion of the oil has been shown[3] to consist of myrcene, phellandrene, citral and the methyl ethers of eugenol and chavicol. According to Power and Kleber, the reported finding of α-pinene by Mittmann[4] is in error.

In connection with a general survey of the industries of the Virgin Islands, a reinvestigation of this oil was deemed desirable.

In the present investigation use was made of a pressure controlled vacuum-fractionating assembly described later, whereby a more effective separation of the constituents of bay oil than that indicated in previous reports was made possible. Systematic examination of the fractions so obtained shows the oil to be more complex than heretofore believed, and the information in the literature regarding the composition of the oil is in need of revision in several particulars.

The presence of myrcene, citral and phellandrene was confirmed without much difficulty, although the physical properties of myrcene would seem to be somewhat different from those previously reported. Present findings show definitely, however, that the non-phenol portion of the oil contains several constituents not previously stated to be present. These include small quantities of α-pinene, substantial proportions of cineol, and of dipentene (with some limonene), the latter an integral part of the oil. It is presumed that dipentene obtained by Power and Kleber in one of their experiments was regarded by them as an isomerization product of one of the other constituents, since these authors did not include their finding of the dipentene in the summary of constituents.

Methyleugenol and methylchavicol, thought by them to be present in appreciable quantities, if present at all in the true *Pimenta acris* oil, are there only in traces as shown by methoxyl determinations of appropriate fractions. A very small quantity of a geraniol-like alcohol is also present, but its identity was not determined.

Contrary to the belief that only one optically active substance is present in bay oil (α-phellandrene), repeated fractionation shows definitely that there are at least four, three of which are positive and one negative, the

(1) Presented before the Division of Medicinal Chemistry, Denver Meeting of the American Chemical Society, September 22–26, 1932.

(2) "The Volatile Oils," Gildemeister and Hoffmann, Vol. III, 1922, pp. 193–194.

(3) Power and Kleber, *Pharm. Rundschau*, **13**, 60 (1895).

(4) Mittmann, *Archiv. Pharm.*, 529–548 (1889).

latter sufficiently predominating in effect to give the oil as a whole a negative rotation.

The various constituents found by way of fractionating the *phenol free* portion of the oil were also characterized from appropriate fractions of the *whole bay oil* (the whole oil without preliminary removal of the phenols) when similarly fractionated (data obtained on the latter are not included here). The properties determined on fractions of the whole oil, such as densities, refractive indices and rotations, corroborated previous findings.

Experimental Part

Through the coöperation of Mr. C. L. Horn of the St. Thomas Agricultural Experiment Station and Mr. E. V. Roberts of the Forest Service a 1600-g. sample of authentic bay oil was procured.

The oil was obtained from the fresh green leaves of *Pimenta acris* collected in St. John and prepared by steam distillation in the usual manner, the yield of oil being about 1.22%.

The oil had the following properties: n_D^{20} 1.5134; $d_4^{15.5}$ 0.9796; α_D −2.4° (100 mm.); aldehyde as citral (Kleber method), 2.0%; total phenol (by volume), 58.4%.

Separation of the Phenol from the Non-phenol Portion.—It is rather difficult to prepare the non-phenol portion of bay oil entirely free from phenol. In order to effect a complete separation, the following special precautions were taken. The bay oil (1500 g.) was extracted with an excess of 5% sodium hydroxide solution until shown to be phenol free by testing small portions of the alkaline washings with (diazotized) *p*-nitroaniline.[5] (The test is particularly delicate for eugenol.) The non-phenol oil was then thoroughly freed from alkali by washing first with *cold* tenth normal sulfuric acid, and then by a series of successive washings with cold water until the washings were neutral. The alkali phenolate solution was carefully extracted a number of times with ether to effect the recovery of small quantities of non-phenol oil dissolved by the phenolate.

The ethereal extract, after a similar washing, was distilled to remove the ether, the residual oil was again washed with alkali to remove traces of phenol and then with acid, water, etc., as before, and this oil added to the bulk of oil. The total non-phenol oil, after drying over anhydrous sodium sulfate and filtering, weighed 525 g.

In view of the wide difference in boiling points of the constituents, the sample used for the fractionation (500 g.) was given a preliminary distillation under reduced pressure and separated into two fractions of convenient boiling range, the first 342 g. distilling up to 68° at 20 mm. and the remainder distilling above this point. During the fractionation proper the second portion was added when the appropriate distillation temperature (68° at 20 mm.) was reached.

Fractionating Apparatus

A. Large Fractionating Assembly.—A wire gauze plate rectifying column (32 plates, 5 cm. inside diameter, 200 cm. in height) which is an improved form of this type of column described by the author in previous publications.[6]

Thermal insulation for the column was provided by an electrically heated jacket, which was divided into five separate circuits, each rheostat controlled.[7] Thermometers

(5) Palkin and Wales, THIS JOURNAL, **46**, 1488 (1924).

(6) Tech. Bull. 276, U. S. Department of Agriculture; *Ind. Eng. Chem.*, **25**, 95 (1933).

(7) Bruun, *Bur. Standards J. Research*, **7**, 851 (1931).

were placed at appropriate intervals in the space between the column and jacket tubes to show temperature gradient.

The superior efficiency of lagged over unlagged columns has been shown by Marshall and Sutherland.[8]

A steel waste-paper basket, with the bottom cut out and lined with asbestos served as a jacket for the distillation flask.

Pressure in the system was maintained constant by means of a short inclined mercury regulator and relay, described in a previous publication.[6] Virtually all the distillations were carried out at 20 mm. or less.

B. **Small Fractionating Assembly.**—This assembly was in its general plan, including the plate column (20 plates and about 120 cm. in height), like the large one. Details of its construction are given in the earlier publication.[6]

Fractionation.—In general the bulk of the sample was fractionated in the large (32-plate) column and the last 60 to 80 g. transferred to the smaller column to complete the fractionation. The fractions so obtained were examined for density, refractive index, rotation, etc., and in most instances refractionated twice (in some instances after the removal of citral and cineol), and the physical constants determined in each case for the new fractions. Refractionation was carried out in a systematic fashion. Since pressure was carefully controlled throughout all the distillations, distillation temperature served very satisfactorily as a guide to indicate the appropriate time for adding, during the course of distillation, the successive fractions from the previous series.

As the total number of fractions involved is very large, only such fractions are tabulated (Tables I, II and III) as show significant changes in properties—maxima or minima in density, refractive index and rotation. The intermediate fractions which exhibited properties in between those listed are omitted.

The first fractionation gave fractions 1 to 24 and these in turn were refractionated giving the series 1A to 32A.

Since the properties of the first series of 24 fractions are reflected in those of the refractionation (Series 1A–32A) with the corresponding maxima and minima more marked, no space is taken to tabulate the data on the first series.

Table I gives the data on the significant fractions of the A series.

TABLE I

DATA ON SIGNIFICANT FRACTIONS OF THE A SERIES OBTAINED BY REFRACTIONATION OF THE FIRST SERIES (1 TO 24)

Fraction	Dist. temp., °C.	Mm. press.	Wt., g.	n_D^{20}	Density 15.5°	α_D Angular rotation	Dominant constituent	
1A	53–55	20	2	1.4619	0.8522	+19.7	α-Pinene	
2A	55–62	20	4	1.4633	.8366	+15.2		
5A	65–65.2	20	31	1.4656	.7977	+ 2.6	Myrcene	
6A	65.2	20	20	1.4657	.7979	+ 2.6	Myrcene	
12A	66.2–67.2	20	15	1.4672	.8130	+ 5.8	Phellandrene	+ Cineol Citral
18A	70.5–70.7	20	16	1.4665	.8702	−25.9	Dipentene and Limonene	+ Cineol Citral
23A	53.4–66	7	8	1.4738	.8421	− 8.3		
25A	74.4–76	7	8	1.4625	.8728	−10.6		
29A	88–91.4	7	7	1.4785	.9219	+ 4.3	An alcohol	
32A	96 up	1	16	1.4864	.9098	0		

A graph showing the rotation data of the series is given in Fig. 1.

(8) Marshall and Sutherland, *Ind. Eng. Chem.*, **19**, 735 (1927).

Of this series, 4A to 23A (inclusive) were again refractionated, giving the new series of fractions designated 4B to 25B. Fractions 1A to 3A (inclusive) were too small to be

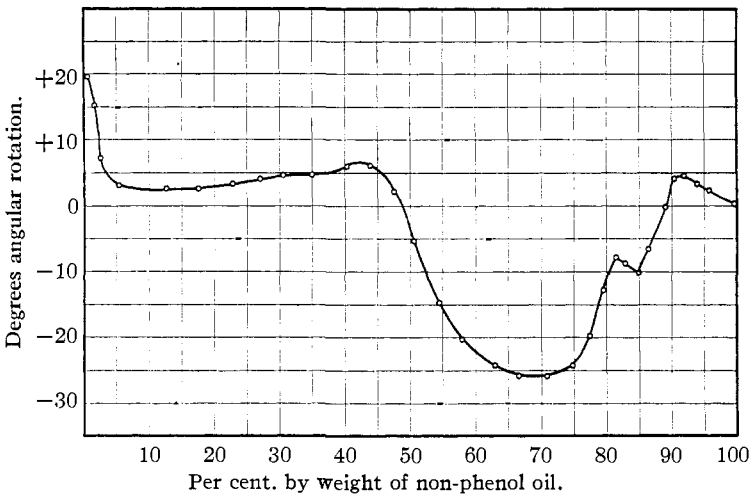

Fig. 1.—Observed rotation of non-phenol portion of bay oil.

included in this refractionation. This was also the case with fractions 24A to 32A (inclusive) after being deprived of citral as described later. Data on the significant fractions of this series are given in Table II.

TABLE II

DATA ON SIGNIFICANT FRACTIONS OF THE B SERIES OBTAINED BY REFRACTIONATION OF 4A–23A

Fraction	Dist., temp., °C.	Press., mm.	Wt., g.	n_D^{20}	Density 15.5°	α_D Angular rotation	Dominant constituent
5B	65–65.2	20	18	1.4649	0.7973	+ 2.2	Myrcene
6B	65.2–65.4	20	14	1.4650	.7966	+ 2.5	Myrcene
12B	66–66.2	20	12	1.4674	.8079	+ 7.6	Myrcene and Phellandrene
13B	66.2–67.8	20	15	1.4673	.8224	+ 6.7	Phellandrene
19B	70.6	20	20	1.4666	.8684	−26.4	Dipentene and Limonene + Cineol
20B	70.6–70.7	20	15	1.4668	.8663	−27.2	Dipentene and Limonene
25B	51	1.5	10	1.4727	.8397	− 8.7	

Cineol was removed from fractions 12B to 24B as described later, and the cineol free fractions were refractionated, giving the series 1C to 9C.

Data on the significant fractions of this series are given in Table III.

In view of the prolonged period over which fractionation had to be made, some polymerization (myrcene and phellandrene both tend to polymerize) was unavoidable even at the comparatively low temperatures involved. The polymer dimyrcene was indicated toward the end of the distillation.

Removal of Aldehyde.—Fractions 24A to 32A gave a positive qualitative reaction for aldehyde when tested in an alcoholic solution with a few drops of fuchsine reagent. An alcohol blank was used for control. These aldehyde-containing fractions were ex-

TABLE III

SIGNIFICANT FRACTIONS OF THE C SERIES OBTAINED BY REFRACTIONATION OF 12B–24B AFTER REMOVAL OF CINEOL

Fraction	Dist. temp., °C.	Press., mm.	Wt. in g.	n_D^{20}	Density 15.5°	α_D Angular rotation	Dominant constituent
1C	65.5–67	20	9	1.4682	0.8192	− 2.8°	
7C	70.2	20					
	to 49	7	10	1.4704	.8568	−31.7°	Dipentene and Limonene
8C	49–51.2	7	10	1.4727	.8519	−35.8°	Dipentene and Limonene
9C	Residue in col.	1	7	1.4765	.8429	−33.5°	Dipentene and Limonene

tracted several times with bisulfite solution, washed free from the reagent and used for subsequent examination. The aldehyde was liberated from the bisulfite compound and identified as described under citral.

The total residual oil left from 24A to 32A after removal of aldehyde was too small to permit refractionation.

Removal of Cineol.—Fractions 12B to 24B, which had a strong eucalyptol-like odor, were extracted several times with 50% resorcinol as described later under cineol. The residual cineol-free oil was thoroughly washed with water until free from resorcinol as shown by ferric chloride tests of the washings, dried and refractionated, giving the series of fractions 1C to 9C of Table III as previously mentioned.

Examination of the Fractions

α-Pinene (Fractions 1A and 2A).—The nitrosyl chloride. In view of the very small quantity available for this examination, details of the procedure used for the preparation of the nitrosyl chloride with but 1 cc. of oil are here given as follows (adapted from the modified Lynn procedure).[9] A mixture of 1 cc. of the oil (fraction 1A), 1 cc. of 95% alcohol and 1 cc. of ethyl nitrite in a test-tube was well cooled in an ice-bath and to it was added, drop by drop, with vigorous stirring, 0.85 cc. of 8 *N* alcoholic hydrochloric acid. After standing for about one hour in the ice-bath with occasional shaking, the precipitate was filtered off by suction, using a micro filtering arrangement, and washed. The dry precipitate was purified in the usual manner by dissolving it in a minimum quantity of chloroform and adding methanol, crystallization taking place almost immediately; m. p. 104–105°.

This is the nitrosyl chloride of the inactive form, which comes out first.

Myrcene (Tetrabromide of the Dihydromyrcene).—Dihydromyrcene was prepared from fraction 4B by reduction with sodium and alcohol and then converted to the tetrabromide, in general as described by Enklaar.[10]

Recovery of the tetrabromide from the oily by-products by the Enklaar method was virtually impossible. The following procedure yielded an excellent crystallization. (a) The oily layer obtained by pouring the brominated reaction mixture into water was drawn off in a separatory funnel (without preliminary dissolving in ether), and washed several times with sodium carbonate solution, then with water. (b) The acid aqueous layer was extracted with ether. The ethereal layer was washed as above, the bulk of the ether evaporated in vacuum, and the residual oil was combined with the original oil from (a). The total oil was then shaken several times with *cold* 95% alcohol, which is a good solvent for the oily by-products and with which the tetrabromide formed an immiscible layer. The tetrabromide thus purified, on dissolving in warm absolute alcohol and allowing to stand, gave excellent crystals. The product, after one recrystallization from absolute alcohol, melted sharply at 88°.

(9) Lynn, THIS JOURNAL, **41**, 361 (1919).

(10) Enklaar, *Rec. trav. chim.*, **26**, 164 (1907).

Purification of Myrcene

Previous reports on myrcene by Power and Kleber[3] and Enklaar,[10] show that these authors found this compound optically inactive or nearly so, density at 15°, 0.8013 and refractive index 1.4700.

Attempts were made to prepare a pure optically-inactive myrcene by fractional crystallization of the myrcene fractions, liquid air being used as a refrigerant, since repeated fractional distillation did not yield the hydrocarbon entirely free from optical activity. The "freeze" produced, however, was very sirupy, too thick to permit filtration. It is presumed that the persistent optical activity in myrcene fractions is due to α-phellandrene.

The inactive myrcene obtained by Power and Kleber and Enklaar may, perhaps, be accounted for by the presence of nearly balanced proportions of phellandrene (positive rotation) and limonene (negative rotation). The minimum density (see Table II) of the myrcene obtained in this investigation would seem, if anything, to indicate a higher purity than that previously reported since both compounds, α-pinene immediately preceding and α-phellandrene immediately following myrcene in the fractionation, have considerably higher densities.

The properties of this compound are accordingly as shown in Table II, fraction 6B: $d_4^{15.5}$ 0.7966; n_D^{20} 1.4650, b. p. 65–66° (20 mm.) and 166–167° (760 mm.).

Phellandrene.—The nitrosite was prepared from fraction 12B by treating a well-cooled mixture of 5 cc. of the oil in about 15 cc. of petroleum ether and 5 cc. of a saturated solution of sodium nitrite with glacial acetic acid, drop by drop, until about 5 cc. of the acid was added—shaking continuously. A pasty mass was obtained, which after the supernatant liquid was poured off was washed by kneading several times in cool water, the wash water being poured off. This mass was then taken up in methanol, the yellow precipitate so obtained filtered, washed several times with small quantities of cold methanol and then recrystallized from chloroform and ether; m. p. 104–105°.

Several attempts were made to prepare a nitrosyl chloride from these fractions, but none was obtained, showing apparently that α- and not β-phellandrene is here involved.[11]

Cineol (Fractions 12B to 24B).—(a) Cineol hydrobromide was prepared by allowing gaseous hydrobromic acid to flow over (rather than through) a petroleum ether solution of the oil well-cooled in an ice-bath while shaking gently to facilitate absorption of the gas. The crystalline mass was then filtered by successive washing with petroleum ether and dried; m. p. 56–57°.

(b) **Cineol-Resorcinol. Addition Compound.**—The oil when shaken with 50% resorcinol solution became practically a solid crystalline mass. The crystals after filtration and washing with water and then with petroleum ether and drying, had a melting point 79–80°. The cineol, regenerated in the usual manner, possessed the characteristic odor of this compound.

Citral (Fractions 24A to 32A).— The oil was treated in the usual way with cold concentrated sodium bisulfite solution. Only the fresh reagent prepared by passing sulfur dioxide through a saturated solution of sodium carbonate was found effective. Some of the fractions rich in citral, when treated with the bisulfite, became a solid crystalline mass. The citral was regenerated from the well-cooled bisulfite with alkali in the usual manner. It possessed the characteristic odor and gave with β-naphthylamine and pyruvic acid the characteristic yellowish β-naphthylcinchoninic acid which on recrystallization from alcohol melted at 195°.

Dipentene and Limonene (Fractions 5C to 9C). (a) **Tetrabromide.**—No difficulty was encountered in preparing the tetrabromide by the Godlewski procedure.[12] The product was subjected to fractional crystallization in an effort to prepare the limonene

(11) Francesconi and Sunagiotto, *Atti accad. Lincei*, [V] **20**, 1, 325 (1911).

(12) Godlewski, *Chem.-Ztg.*, **22**, 827 (1898).

tetrabromide, but this was not accomplished on account of the predominating proportions of dipentene; m. p. tetrabromide 123–124°.

(b) **Nitrosyl Chloride.**—A nitrosyl chloride was prepared by the method described for α-pinene with the exception that glacial acetic acid was also added in addition to the alcoholic hydrogen chloride. The somewhat pasty mass produced at first became crystalline on addition of the acetic acid; melting point of limonene nitrosyl chloride 103–104°.

Nitrosite.—In view of the belief that the negative rotation of bay oil was due to α-phellandrene,[3] an effort was made to prepare a nitrosite from fraction 9C but without success. Phellandrene was identified only in positive fractions immediately following the myrcene.

An Alcohol (Unidentified).—Fractions 28A to 32A, after removal of citral, possessed a very pleasant geraniol- or nerol-like odor. These fractions, after removal of citral, were very small (a few grams total). An approximate estimation of the alcohol content of 32A, on about 0.4 g. showed this fraction to contain about 23% alcohol calculated as $C_{10}H_{18}O$. A separation of the alcohol from the indifferent oil on the combined fractions 28A to 32A was made by way of the boric acid esters, the Schmidt procedure,[13] being used. The yield of ultimate "alcohol" was very small.

No crystalline phenylurethan or diphenylurethan could be isolated. The oil, however, gave a pronounced violet-red color reaction with alcoholic hydrobromic acid and with concentrated sulfuric acid similar to that obtained by Erdmann and Huth[14] for rhodinol and linalool.

Methylchavicol and Methyleugenol.—Anise-scented fractions, reported by previous investigators, were not encountered in any of the fractionations.

A determination of methoxyl on 24A, 28A and 32A by the modified Vieböck and Schwappach method,[15] 30–50 mg. being used for a determination, showed a methoxyl content as follows: 24A—0.41%; 28A—1.08%; 32A—4.71%. Since these fractions totaled but a few grams, the maximum content of methyl ethers in the original bay oil, if present at all, would seem to be negligible. The quantities in the fractions were too small to permit identification.

Oil from the anise-scented variety of *Pimenta acris* has been shown by Warneford[16] to contain about 15% estragol (methylchavicol).

In the usual harvesting of bay leaves by the natives, an admixture of leaves from the anise-scented and limoncilla varieties is almost unavoidable unless collected under the careful supervision of an experienced botanist. It is barely possible that the bay leaves used by Power and Kleber[3] contained appreciable quantities of the anise-scented variety, and this may account for their findings with regard to the methyl ethers.

Esters.—Fractions 28A to 32A possessed a rather sweet odor. It was thought that this might, in part, be ascribable to an ester. Saponification of small samples with alcoholic potash in the usual manner indicated no more than a trace to be present.

Acknowledgment.—The authors are pleased to acknowledge their indebtedness to Dr. W. W. Skinner for his many valuable suggestions during the progress of this work.

Summary

With the aid of an improved vacuum fractionating assembly, here described, oil of bay has been subjected to a more critical examination than heretofore.

(13) Schmidt, *Chem.-Ztg.*, **52**, 898 (1928).
(14) Erdmann and Huth, *J. prakt. Chem.*, **56**, 4 (1897).
(15) Clark, *J. A. O. A. C.*, **15**, 136 (1932).
(16) Warneford, *Trop. Agri. (Trinidad)*, **4**, 128 (1927); *C. A.*, **22**, 2238 (1928).

The present investigation, relating to the non-phenol portion of the oil, shows that previous conclusions regarding its composition are erroneous in several particulars.

The following composition is indicated: myrcene, cineol and dipentene, with limonene are the predominating constituents; citral, a small amount of α-phellandrene and, contrary to previous reports, a small amount of α-pinene and but little, if any, methylchavicol and methyleugenol are present. A small amount of a geraniol-like alcohol was also found, but its identity was not determined.

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Crystallizable Chavicol and Eugenol from the Oil of Bay[1]

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As indicated in another paper[2] the major portion of the oil of bay (obtained by steam distillation of the leaves of *Pimenta acris*) consists of phenols.

As early as 1877 Markoe[3] had already observed the presence of eugenol in the "heavy oil of bay."[4] This term is applied to the oil coming over in the latter part of the distillation, which is rich in phenols.

Mittmann,[5] who made an examination of the whole oil, concluded that eugenol was the only phenol present, but Power and Kleber,[6] in a more comprehensive investigation of the oil, established the presence of another phenol, namely, chavicol. These authors were unable to separate the phenols as such but proved the presence of chavicol and eugenol by converting the total phenol portion to the methyl ethers and fractionating these.

So far as we are aware, however, chavicol as such has never been isolated from the oil of bay nor has the pure eugenol been prepared from this source.

In a recent investigation of the composition of bay oil, fractionation of the phenol portion with the aid of pressure-controlled plate columns made possible a very effective separation of the two phenol constituents. The chavicol fractions so obtained in one fractionation solidified to a beautiful crystalline mass on moderate cooling.

(1) Presented before the Division of Medicinal Chemistry, Denver Meeting of the American Chemical Society, September 22–26, 1932.

(2) Palkin and Wells, THIS JOURNAL, **55**, 1549 (1933).

(3) Markoe, *Proc. Am. Pharm. Assoc.*, p. 438 (1877).

(4) This term is applied to the oil coming over in the latter part of the distillation, which is rich in phenols.

(5) Mittmann, *Ber.*, **27**, 352 (1894).

(6) Power and Kleber, *Pharm. Rundschau*, **13**, 60 (1895).