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.

WASHINGTON, D. C.

RECEIVED AUGUST 19, 1932
PUBLISHED APRIL 6, 1933

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

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

BY S. PALKIN AND P. A. WELLS

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)

Eykman[7] cooled chavicol which he purified from betel oil to −25° without effecting crystallization.

By repeated fractional distillation and fractional crystallization, both chavicol and eugenol were prepared in a high state of purity and their physical properties determined.

Experimental Work

Preparation of the Phenol Portion.—The general procedure for the separation of the non-phenol portion of bay oil from the phenols is described in the other publication.[2] To recover the phenols, the solution of alkali phenolate so obtained was well cooled, and the phenols were liberated with 10% sulfuric acid (a slight excess). The bulk of the oil was separated by centrifuging, and the oil dissolved in the water was obtained by extraction with ether. Both the bulk of phenol oil and the ethereal extract were thoroughly washed with water until free from acid. The ether was distilled off in vacuum, the phenol residue from this added to the main portion of phenol, and the moisture removed by distillation in vacuum. The proportion of eugenol in the total phenol, obtained by way of a methoxyl determination, was found to be 89.3%, or the chavicol content, by difference, 10.7%.

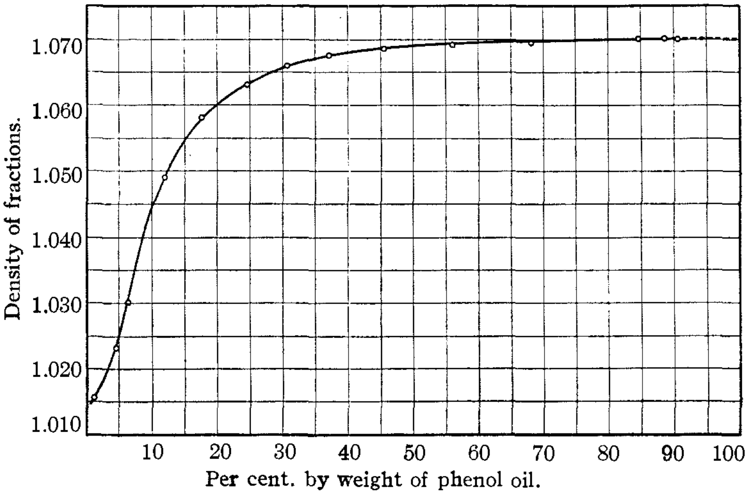

Fig. 1.—Density of phenol portion of bay oil.

Fractionations.—The phenol oil (900 g.) was fractionated in a large 32-plate column at 7 mm. up to the last 100 g., fractionation of the latter being completed in the small 20-plate column. The density and refractive index were taken for each fraction. The series of fractions so obtained distilled between 105.4 and 114°. The density (Fig. 1) and refractive index gave no indication of other phenols.

The plate column assemblies used in this investigation are described in another paper in THIS JOURNAL.[3]

Preparation of Pure Chavicol.—For further purification of chavicol, the first fractions were systematically refractionated. Of eleven fractions so obtained the first nine were again refractionated.

---

(7) Eykman, *Ber.*, **22**, 2739 (1889).

Fractional Crystallization.—The fractions distilling between 103.2 and 103.6° at 7 mm. (density ranged from 1.0190 to 1.0200 and refractive index from 1.5426 to 1.5436) were combined and subjected to five crystallizations. The solid portion of the fifth was again fractionally distilled and examined for density, refractive index, quantity of methoxyl, etc.

The chavicol thus prepared had the following properties: m. p. 16°; b. p. 235–236°; n^{20}_{D} 1.5448; $d^{15.5}_{4}$ 1.0203; methoxyl (0.050 and 0.048% or 0.26% calculated as eugenol). On this basis the chavicol is over 99.7% pure.

Determination of methoxyl was found to be a convenient guide in following the purity (pertaining to freedom from eugenol) of the chavicol.

The technique involved in the crystallization was somewhat as follows. A jacketed Gooch filtration arrangement was used, the upper half of an ether can serving as a jacket, and a crucible with a coarse sintered glass bottom (No. 1 or 2) as the filtering device. A few pieces of ice in the jacket provided sufficient insulation. The sample to be recrystallized was cooled in an ice and salt bath to the consistency of a "slush" by stirring vigorously while in the cooling bath. This was then transferred to the filter device and moderate suction applied as soon as the filter plate was fully covered. Care must be taken in this operation to keep the crystalline portion pressed down to a compact mass in the crucible, as otherwise channeling occurs, warm air is pulled through, and it is not possible to suck the mass dry.

Chavicol 3,5-dinitrobenzoyl ester was prepared without any difficulty by the method of Phillips and Keenan,[8] m. p. 103.5–104.5°.

Purification of the Eugenol.—Of the first fractionation of the original mixture of phenols, the last five fractions distilling between 113.8–114° at 7 mm. were practically all eugenol, the properties of the fractions corresponding well with those reported for eugenol from other sources. The density ranged from 1.0690 to 1.0701, and the refractive index from 1.5403 to 1.5405.

These were combined and fractionally distilled, then fractionally crystallized, more or less as described for chavicol, and again distilled in vacuum. Solid carbon dioxide was used as the refrigerant instead of ice. Properties of purified eugenol so prepared are as follows: m. p. −7.5°; b. p. 254°; n^{20}_{D} 1.5405; $d^{15.5}_{4}$ 1.0701; methoxyl, 18.79%; calcd., 18.92%. The 3,5-dinitrobenzoyl ester prepared as described above had a melting point of 130–131°.

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

By means of repeated fractional distillation and fractional crystallization of the phenol portion of bay oil, chavicol and eugenol of high purity were obtained, which crystallized at +16 and −7.5°, respectively.

The method of preparation used and data on the properties of the purified phenols so obtained are given.

WASHINGTON, D. C.

RECEIVED AUGUST 19, 1932
PUBLISHED APRIL 6, 1933

---

[8] Phillips and Keenan, THIS JOURNAL, **53**, 1924 (1931).