

## PHYTOCHEMICAL NOTES.\*

## 73. OIL FROM MENTHA CITRATA.

---

R. C. ROARK.

---

Volatile oils of various species of mint have long been known and are used in large quantities, but the oil obtained from *Mentha citrata* Ehrh. appears to have received but little attention until comparatively recently.

In the Cyclopedica of American Horticulture, 1903, in the article "Mentha" by Lyster H. Dewey, this statement appears, following a botanical description of the *Mentha citrata*—"The fragrant lemon-scented oil is distilled for use in making perfumes."

In the Report of Schimmel & Co., for April, 1904, p. 95, there is an account of a chemical examination of the oil from this plant. The yield of oil from young, not flowering, but fresh plants, without roots, was about 0.2 p. c. The oil was of a pale yellow color, had an odor suggestive of lavender oil, and possessed the following constants:  $d_{15}^{\circ}=0.8826$ ;  $n_D^{\circ}=-5^{\circ}35'$ ; ester number=31.28, corresponding to 10.95 p. c. linalyl acetate; soluble in two and more volumes of 70 p. c. alcohol. From the same plant a distillate was obtained from the frozen leaves in about the same yield. The constants of this oil were  $d_{15}^{\circ}=0.8895$ ;  $n_D^{\circ}=-1^{\circ}41'$ ; ester number=111.28, corresponding to 38.95 p. c. linalyl acetate; soluble in two and more volumes of 70 p. c. alcohol.

In the exhibit<sup>1</sup> of E. Moulié at the Florida State Fair, Tampa, 1906, there were samples of the "dried *Mentha citrata* flowers (No. 10); "powdered *Mentha citrata* leaves, for sachet bags" (No. 7); "pomade, by enfleurage, of the *Mentha citrata* leaves for blending and coloring purposes" (No. 26); "pomade, by enfleurage, of the *Mentha citrata* leaves for blending and perfuming purposes" (No. 27); "cohobated water distillate of *Mentha citrata*" (No. 32); "volatile of *Mentha citrata* (Bergamot mint) on its water distillate" (No. 41), and finally a "stock syrup of *Mentha citrata*" (No. 47). In the descriptive catalogue of this exhibit it is stated by Moulié that the volatile oil of *Mentha citrata*, or Bergamot mint as it is sometimes called, was "originated" in 1892.

For several years *Mentha citrata* has received the attention of Dr. R. H. True and his collaborators in the Bureau of Plant Industry. It was at the suggestion of Dr. True that roots, sent from Washington, were planted in the garden of the Northern Station for the Cultivation of Medicinal Plants at Madison. As a result, a very small amount of oil was distilled during the summer of 1909,<sup>2</sup> but not enough to work with. During the summer of 1910 a somewhat larger amount of oil was distilled.<sup>3</sup> Although insufficient for a thorough investigation, it sufficed for a preliminary examination.

The oil had a clear yellow color, an intense but rather pleasant odor, and had the following properties, viz.,  $d_{22}^{\circ}=0.895$ ; refractive index at  $19.5^{\circ}=1.4555$ ; optical rotation in a 200 mm. tube= $-17^{\circ}.6$ .

Small amounts of oil, 5 cc., were shaken with a 30 p. c. solution of sodium

---

\*From the laboratory of Edward Kremers.

<sup>1</sup>Descriptive catalogue of the Franco-American Florida Floral Perfumery.

<sup>2</sup>See Report for 1909, made by the Agent to Dr. True.

<sup>3</sup>See Report for 1910, made by the Agent to Dr. True.

bisulphite; two samples were treated at room temperature and two others were heated in a simmering water bath, for about 20 minutes. After standing some time the resulting volume of oil was read in an ordinary cassia flask.

The results were as follows:

- 5 cc. of oil heated with bisulphite solution, vol.=4.85 cc.
- 5 cc. of oil heated with bisulphite solution, vol.=4.80 cc.
- 5 cc. of oil treated with bisulphite solution at room temperature, vol.=4.85 cc.
- 5 cc. of oil treated with bisulphite solution at room temperature, vol.=4.80 cc.

Percentage of aldehydes=3.50 p. c. The above results indicate that it apparently makes no difference whether the aldehydes are shaken out either at room temperature or at the temperature of a water bath.

A larger amount of oil, 50 cc., was then treated similarly. The bisulphite was separated from the oil, sodium carbonate added to excess, and the liquid distilled. No oil separated from the distillate, which, however, had a perceptible odor. The oil, shaken out of the aqueous distillate, had a very pleasant ethereal odor and was very volatile, passing off with the ether vapor.

The oil from which the aldehydes had been removed by the bisulphite solution, was washed carefully with a dilute solution of sodium carbonate, then with distilled water, and finally dried. Portions of this oil were saponified by boiling with an excess of approximately N/2 alcoholic potassa for 30 minutes on the water bath in a flask fitted with a reflux condenser.

- (1) 1.71 grams oil required for saponification 0.2694 g. KOH. Sap. No.=230.0.
- (2) 0.882 grams oil required for saponification 0.2071 g. KOH. Sap. No.=234.7.

Computed as linalyl acetate this corresponds to from 80.50 to 82.15 p. c.

The whole of the oil was then saponified in the same way. After saponification, the odor of the oil was changed, a lavender-like odor being noticed. The saponified oil in a 100 mm. tube gave an optical rotation of  $-15^{\circ}.85$ .

The saponified oil was removed from the excess of alkali by steam distillation and was separated, washed, and dried in the usual manner. The amount of oil was too small for fractionation. A portion, 10 cc., of this oil was acetylated by boiling for 3 hours with an equal volume of acetic acid anhydride, with the addition of a gram or so of anhydrous sodium acetate, in an acetylation flask. After acetylation, the oil had an odor still more suggestive of that of lavender oil.

The acetylated oil was separated, washed thoroughly with a dilute solution of sodium carbonate and with distilled water, and then dried. Portions of this oil were saponified with the following results:

- 1.741 grams oil required for saponification 0.3175 g. KOH. Sap. No.=182.
- 1.759 grams oil required for saponification 0.3259 g. KOH. Sap. No.=185.

Computed as linalyl acetate this corresponds to from 63.70 to 64.75.

Although the presence of linalyl acetate has only been assumed and not at all proven, this discrepancy between the original ester content and the lower ester content of the acetylated oil is in harmony with the assumption of the presence of linalool, which is partly decomposed by the acetic acid anhydride during the acetylation process.

The alkaline solution from which the saponified oil had been removed by steam distillation, was diluted, acidified with sulphuric acid, and again subjected to steam distillation. A strong odor of sulphur dioxide was noticed, thus revealing that some of the aldehyde hydroxy sulphonate had not been removed by washing. A small amount of oil collected on the surface of the distillate. Barium

carbonate was added in excess, the precipitate filtered off, the filtrate evaporated to a small bulk, again filtered, and allowed to evaporate to dryness over sodium hydroxide. Leaf-like crystals were deposited. These were dissolved in a small quantity of hot water, the solution filtered, and after the addition of a drop of dilute nitric acid, silver nitrate was added. This precipitated a salt which in a few seconds turned brown and then black. This mixture was heated, the black substance was filtered off, and upon chilling the filtrate, a white salt was obtained. This salt was unstable, turning dark upon standing. The salt was filtered off, dried on porous plate over sulphuric acid, and the silver determined as silver chloride.

0.1006 g. salt gave 0.0858 g. silver chloride.

Percentage of silver in salt=64.24.

Calculated for silver acetate=64.66.

The solution of the barium as well as of the silver salt in hot water had a distinct fatty acid odor, thus indicating the presence of at least traces of other acids.

---

#### PHYTOCHEMICAL NOTES.\*

##### 78. AN UNUSUAL OIL OF WORMWOOD.

---

R. C. ROARK.

---

Several years ago there was left at the laboratory a sample of oil of wormwood by Mr. Leander Drew, the well-known wormwood distiller of Sauk Co., Wisconsin. For more than half a century wormwood has been cultivated and distilled in Sauk Co. by three generations of the Drew family. This sample of about a pound had been set aside by Mr. Drew because of its unusual density. Mr. Drew could not account for the peculiarity of the sample which in other respects resembled the general run of oil of the same still and season.

The specific gravity of the oil determined by means of a Mohr-Westphal balance at 21.5° was found to be 1.000. The usual density of wormwood oil is supposed to vary between 0.925 and 0.955<sup>1</sup>

The saponification number was first ascertained in the usual manner by boiling about 2 grams with 20 cc. N/2 alcoholic potassium hydroxide solution for 40 minutes. Two determinations yielded 151 and 150 respectively as saponification numbers.

Owing to the dark color of the reaction mixture, the method of saponification was modified in a manner that has proven effective on previous occasions. About 5 grams of oil were heated with 50 cc. of N/2 alcoholic potassium hydroxide solution for 90 minutes. The saponification mixture was transferred to a 500 cc. measuring flask and diluted with water so that the oil rose above the mark in the neck of the flask, thus yielding exactly 500 cc. of aqueous alkaline liquid. The reaction mixture thus diluted was next transferred to a separating funnel and the aqueous portion was drawn off through a filter. Of the filtrate, portions of 100 cc. were used for titration with standard acid. The dark oil being thus

---

\*From the laboratory of Edward Kremers.

<sup>1</sup>G. H. K., The volatile oils, p. 685.