

SCIENTIFIC SECTION

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A STUDY OF SEVERAL SPECIES OF THE GENUS *MONARDA*.*¹

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1—THE VOLATILE OILS OF THE *MONARDAS*.

During the progress of the study of several species of the Genus *Monarda*, oils from some of them became available in sufficient quantities to determine properties and some constituents. Results of the studies on the oils are given in the first series of papers dealing with the subject of the investigation.

(a) THE OIL OF *MONARDA FISTULOSA* GROWN IN FLORIDA.

Since *Monarda fistulosa* is not native to Florida, the date herewith presented was obtained from oil distilled from plants grown under cultivation in the Medicinal Plant Garden, University of Florida. These plants, in 1930, produced a yield of 0.831 per cent of oil on the green basis.

TABLE I.—CONSTANTS OF *MONARDA FISTULOSA* OIL (FLORIDA, 1930).

Density at 20° C.	0.9382
Refractive Index at 25° C.	1.5000
Per cent Phenols	55.4

These constants agree favorably with those of the Wisconsin oils.

One hundred and fifty cc. of the oil were separated into its component phenols and non-phenols using 5 per cent aqueous potassium hydroxide. After washing and drying these fractions they were fractionally distilled. The following fractions with their corresponding constants were obtained.

TABLE II.—FRACTIONS OF THE PHENOLS AND NON-PHENOLS OF *MONARDA FISTULOSA* OIL (FLORIDA 1930).

Frac-tions.	Boiling Point Range.	Refractive Index at 25°.	Density.
Phenols (Total)		1.5160	0.9382 at 20°
1 Up to 232°		1.5142	0.958 at 20°
2 232° to 236°		1.5180	0.962 at 20°
3 A red resinous residue			
Non-Phenols (Total)		1.4755	0.8641 at 20°
1 Up to 182°		1.4670	0.828 at 25°
2 182° to 192°		1.4751	0.843 at 25°
3 192° to 205°		1.4860	0.857 at 25°
4 205° to 255°		1.4931	0.900 at 25°
5 A red resinous residue			

The various fractions obtained by fractional distillation, as listed above, were examined. The phenols yielded pure carvacrol, m. p. 0.5° C. and b. p. 232° C. to 236° C. Its nitroso derivative melted at 153–154° C. (uncorr.). There was no thymol present.

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The reddish residue from the distillation of the phenols yielded to boiling water, hydrothymoquinone, which crystallized in yellowish needles melting at 141–142° C. A mixed melting point with known hydrothymoquinone gave the same result.

The non-phenols of the lowest boiling fraction yielded a terpene-like substance which failed to yield a crystalline nitroso derivative. It readily absorbed bromine from solution, yielding a colorless oil heavier than water.

Fractions 2 to 4 yielded no derivatives. However, the odors strongly suggested the presence of linalool and geraniol.

SUMMARY AND CONCLUSIONS.

The oil of *Monarda fistulosa* grown in Florida is comparable with the Wisconsin oil in constants and constituents. Neither contains thymol. The constituents are reported as follows:

1. Carvacrol.
2. Hydrothymoquinone.
3. A terpene-like substance with boiling point less than 182°.
4. Possibly geraniol and linalool.

(b) MONARDA MENTHÆFOLIA OIL.

Oil of *Monarda menthaefolia* from plants collected in Wyoming and Colorado in 1931 was obtained by steam distilling the alcoholic extractive obtained from the leaves and stems. After distilling the distillate was cohobated. The constants of the two oils are given in Table III.

TABLE III.—CONSTANTS OF THE OILS OF MONARDA MENTHÆFOLIA (WYOMING AND COLORADO, 1931).

Constants.	Original Oil.	Cohobated Oil.
Density at 20° C.	0.966	0.952
Specific Rotation at 20° C.	1.56	1.57
Refractive Index at 25° C.	1.5110	1.5143
Per Cent Phenols	82.0	93.2

The phenol and non-phenol fractions were separated by means of five per cent aqueous potassium hydroxide. After washing and drying the fractions the following constants were obtained.

TABLE IV.—PHENOLS AND NON-PHENOLS OF MONARDA MENTHÆFOLIA.

Constant.	Phenol Oil.	Non-phenol Oil.
Density at 20° C.	0.969	0.896
Specific Rotation at 20° C.	0.34	1.50
Refractive Index at 25° C.	1.5132	1.4860

The non-phenol oil had a saponification value of 7.39 and an acetyl value of 72.34 corresponding to 21.7 per cent of alcohol and 2.6 of esters.

The non-phenols were next distilled at atmospheric pressure with the following results:

TABLE V.—FRACTIONS OF MONARDA MENTHÆFOLIA NON-PHENOLS.

Fraction.	I.	II.	III.
Quantity	2 cc.	7 cc.	8 cc.
Boiling Point	Up to 182°	182°–205°	Over 205°
Density at 22.5° C.	0.859	0.877	0.909
Specific Rotation at 20°	0	0.45	4.49
Refractive Index at 21.5°	1.4732	1.4799	1.4941

After the separation of the phenols the fraction was chilled below zero. Thymol separated out and was identified by its melting point (m. p. 49.5–50.5° C.). Approximately half of the phenols were thymol.

The mother liquor was separated and was found to congeal at -5° to -11° C. This indicates impure carvacrol. By fractional distillation under reduced pressure pure carvacrol boiling at 140° at 78-mm. pressure was obtained. It melted at 0° C. Its phenyl urethane derivative melted at 134° C.

In the case of the non-phenols, acetic acid was identified in the aqueous distillate of the saponified oil.

By the means of the barium salt of the monosulfonate of cymene containing 24.48 and 24.59 per cent of barium, respectively (the theory is 24.32 per cent), cymene was identified in the fraction distilling below 182° C.

The fraction $182-205^{\circ}$ C. contained 26.63 per cent of an alcohol calculated as $C_{10}H_{18}O$. This was possibly linalool but no derivatives could be prepared.

The fraction boiling over 205° yielded a small amount of geraniol when treated with calcium chloride according to the method of Jacobsen (1).

The distribution of the oil in the plant is shown in Table VI.

TABLE VI.—DISTRIBUTION OF *MONARDA MENTHÆFOLIA* VOLATILE OIL.

Part.	I.	II.	Average.
Flower Heads	0.31	0.30	0.31
Leaves	0.32	0.30	0.31
Stems	0.05	0.05	0.05
Roots	Trace	Trace	Trace

SUMMARY AND CONCLUSIONS.

Oil of *Monarda menthæfolia* in contrast of Oil of *Monarda fistulosa* contains thymol as well as carvacrol. In addition to this the following substances were found:

1. Acetic Acid.
2. Cymene.
3. Geraniol.
4. Probably Linalool.

The constants and various fractions of this oil compare in a measure with the constants of oil of *Monarda fistulosa* but more so with the constants and constituents of the oil of *Monarda punctata*.

(c) OIL OF *MONARDA PECTINATA*, NUTT.

Five pounds of air-dried stems and leaves of *Monarda pectinata* were steam distilled. This material had been collected in Larimer county, Colorado, in 1931. The constants of the oil obtained are as follows:

TABLE VII.—CONSTANTS OF OIL OF *MONARDA PECTINATA*.

Optical Rotation.....	Slightly dextrogyrate
Refractive Index.....	1.5141 at 25°
Density.....	0.9729 at 20°
Phenol Content.....	97 per cent

There was sufficient material available to determine the distribution of the oil in the plant. The results were as follows:

TABLE VIII.—DISTRIBUTION OF *MONARDA PECTINATA* VOLATILE OIL.

Part.	I.	II.	Average.
Flower Heads	0.41	0.40	0.41
Leaves	0.50	0.54	0.52
Stems	0.13	0.11	0.12
Roots	Trace	Trace	Trace

NOTE: Apparatus of Clevenger (2) was used.

The amount of material available did not permit further investigations but the observation was made that the phenol was probably thymol.

(d) OIL OF MONARDA PUNCTATA var. LEUCANTHA.

Monarda punctata var. *leucantha* is common in the vicinity of Gainesville, Florida. Since the establishment of the Medicinal Plant Garden at the University of Florida a number of oils had been collected. These oils were fractionated and examined. In the following tables (IX to XVI) are enumerated the various constants and other data obtained.

TABLE IX.—OIL OF MONARDA PUNCTATA var. LEUCANTHA (1925).

Fractions.	Boiling Point.	Refractive Index at 25°.	Density.
Original Oil		1.5033	0.946 at 20°
Phenols (45 per cent)		1.5142	0.980 at 24°
1	Up to 231°	1.5121	0.949 at 25°
2	231° to 240°	1.5195	0.966 at 25°
3	Residue a red resin		
Non-phenols (55 per cent)		1.4905	0.911 at 24°
1	Up to 182°	1.4718	0.842 at 25°
2	182° to 192°	1.4827	0.857 at 25°
3	192° to 205°	1.4875	0.873 at 25°
4	205° to 255°	1.4987	0.910 at 25°
5	Residue a red resin		

TABLE X.—OIL OF MONARDA PUNCTATA var. LEUCANTHA (1929) WILD PLANTS.

Fractions.	Boiling Point.	Refractive Index at 25°.	Density.
Original Oil		1.4968	0.9218 at 20°
Phenols (24.6 per cent)		1.5170	0.970 at 24°
1	Up to 234°	1.5195	0.934 at 25°
2	Residue a red resin		
Non-phenols (75.4 per cent)		1.4911	0.872 at 25°
1	Up to 192°	1.4790	0.848 at 25°
2	192° to 230°	1.4922	0.884 at 25°
3	Residue a red resin		

TABLE XI.—OIL OF MONARDA PUNCTATA var. LEUCANTHA (1929) CULTIVATED PLANTS.

Original Oil.	Boiling Point.	Refractive Index at 25°.	Density.
Original Oil		1.5108	0.9679 at 20°
Phenols (63.6 per cent)		1.5168	0.970 at 24°
1	Up to 231°	1.4979	0.945 at 24°
2	231° to 240°	1.5161	0.967 at 24°
3	Residue a red resin		
Non-phenols (36.4 per cent)		1.4976	0.927 at 24°
1	Up to 210°	1.4737	0.873 at 25°
2	210° to 255°	1.4957	0.909 at 25°
3	Residue a red resin		

TABLE XII.—OIL OF *MONARDA PUNCTATA* var. *LEUCANTHA* (1930).

Fractions.	Boiling Point.	Refractive Index at 25°.	Density.
Original Oil		1.5012	0.9347 at 20°
Phenols (42 per cent)		1.5160	0.9803 at 20°
1	Up to 231°	1.5166	0.955 at 24°
2	231° to 240°	1.5172	0.966 at 25°
3	Residue a red resin		
Non-phenols (58 per cent)		1.4840	0.8794 at 20°
1	Up to 182°	1.4732	0.823 at 25°
2	182° to 192°	1.4790	0.846 at 25°
3	192° to 203°	1.4840	0.866 at 25°
4	205° to 227°	1.4909	0.887 at 25°
5	227° to 255°	1.4985	0.918 at 25°
6	255° up	1.5057	0.938 at 25°
7	Residue a red resin		

TABLE XIII.—OIL OF *MONARDA PUNCTATA* var. *LEUCANTHA* (1931).

Fractions.	Boiling Point.	Refractive Index at 25°.	Density.
Original Oil		1.5100	0.9695 at 20°
Phenols (65.4 per cent)		1.5163	0.985 at 20°
1	Up to 231°	1.5067	0.953 at 25°
2	231° to 240°	1.5189	0.958 at 25°
3	Residue a red resin		
Non-phenols (34.6 per cent)		1.4978	0.914 at 24°
1	Up to 205°	1.4669	0.852 at 25°
2	205° to 230°	1.4875	0.899 at 25°
3	233° to 255°	1.4978	0.909 at 25°
4	Residue a red resin		

TABLE XIV.—OIL OF *MONARDA PUNCTATA* var. *LEUCANTHA* (1932).

Fractions.	Boiling Point.	Refractive Index at 25°.	Density.
Original Oil		1.5000	0.9276 at 20°
Phenols (44.2 per cent)		1.5169	0.976 at 24.5°
1	Up to 225°	1.5060	0.942 at 25°
2	225° to 228°	1.5162	0.939 at 25°
3	228° to 230°	1.5197	0.9 at 25°
4	230° to 240°	1.5204	0.961 at 25°
5	Residue a red resin		
Non-phenols (55.8 per cent)		1.4859	0.889 at 24.5°
1	Up to 182°	1.4770	0.840 at 25°
2	182° to 192°	1.4814	0.864 at 25°
3	1.92° to 205°	1.4848	0.864 at 25°
4	205° to 255°	1.5004	0.907 at 25°
5	Residue a red resin		

TABLE XV.—OIL OF *MONARDA PUNCTATA* var. *LEUCANTHA* (1933).

Fractions.	Boiling Point.	Refractive Index at 25°.	Density.
Original Oil		1.5029	0.946 at 20°
Phenols (65.6 per cent)		1.5142	0.980 at 24°
1	Up to 230°	1.5051	
2	Residue a red resin		

(Continued from page 15.)

Fractions.	Boiling Point.	Refractive Index at 25°.	Density.
Non-phenols (34.4 per cent)		1.4905	0.911 at 24°
1	170° to 220°	1.4812	
2	Residue a red resin		

By freezing the fractionated phenols in a frigidaire, thymol separated from approximately half of the oils. Therefore, it would appear that this oil would not be entirely satisfactory for crystallizing out thymol by ordinary freezing. Thymol was identified by preparing its nitroso derivative which melted at 161–162° C.

From the supernatant liquid obtained after the crystallization of thymol, carvacrol was obtained. It was identified by means of its nitroso derivative which melted at 153° C.

Hydrothymoquinone was readily isolated from the resins remaining in the distilling flask. After distillation of the phenols, this was accomplished by boiling the resins in water, filtering and allowing the quinone to crystallize from the filtrate. After recrystallization the hydrothymoquinone gave a melting point of 141–142° C. and a mixed melting point with the known substance gave an identical result.

In the non-phenol boiling up to 182° C. a substance was obtained which first formed a solid when treated with amyl nitrite in a cold acidified alcoholic solution and then quickly redissolved and no further precipitation or crystallization was possible. This fraction with potassium permanganate yielded a white crystalline product melting at 190° to 194° C.

The remaining fractions yielded no derivatives although tests were made for linalool and geraniol. There was no aldehyde present.

The distribution of the oil in the plant parts was determined with the following results:

TABLE XVI.—DISTRIBUTION OF *MONARDA PUNCTATA* var. *LEUCANTHA* VOLATILE OIL (1934).

Part.	I.	II.	Average.
Flower Head of September 6	3.6 per cent	3.3 per cent	3.45 per cent
Leaves of September 6	2.0	1.9	1.95
Stems of September 6	0.5	0.6	0.55
Roots of September 6	Trace	Trace	Trace
Flower Head of September 23	2.5	2.7	2.6

NOTE: Apparatus of Clevenger (2) was used.

SUMMARY AND CONCLUSION.

The *Monarda punctata* var. *leucantha* oils show distinct annual variations in their properties. They contain both thymol and carvacrol. Hydrothymoquinone was also isolated.

The presence of terpenes is indicated.

There were no positive tests for geraniol, linalool or aldehydes.

REFERENCES.

- (1) Jacobsen, O., *Ann.*, 157, 234 (1871).
- (2) Clevenger, J. F., *Am. Perf. Ess. Oil Rev.*, 23, 467 (1928).