

## PHYTOCHEMICAL NOTES.\*

## No. 85. The Monarda Oils of 1918 and 1919.

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*Monarda punctata*, 1918.—An oil amounting to 170 grammes was distilled August 25th from the leaves and stems of the plant, chiefly. It was of a rather dark, reddish brown color and had deposited, at the time it was examined eight months later, a crystalline layer. The heptane test (precipitation of hydrothymoquinone) was applied and the density determined, an assay made by the phenol extraction method, and the phenols separated.

Another sample amounting to 90 grammes was obtained from ripe and long dried flower heads. It was rather darker in color than the first.

*Monarda punctata*, 1919.—A quantity of fresh herb in full bloom was distilled October 15th from the Florida variety grown in the Pharmaceutical Garden of the Experiment Station. The yield was 0.1055 percent, which was increased by cohobation to 0.1574 percent. The oil was clear and of a bright brownish color. The density and phenol content of the original oil and each cohobate were determined separately.

A sample cultivated at the Highlands when harvested weighed 95 lbs. It was allowed to dry and distilled after a time. The yield of original oil on the dry basis was 1.496 percent and on the green, 0.645 percent. Cohobation raised that to 2.707 percent. In working up this oil by cohobation a blue aqueous layer was obtained.

Two samples of herb were collected at Lone Rock. The first sample, designated "baled," was collected by mowing the field and raking all of the dried material and baling it in a press. This was distilled at Madison and contained much foreign material; probably one-third was *Monarda*. The yield of oil indicated this also. The yield was increased somewhat by cohobation in this case. The oil was of a pale yellow color with only a slight reddish tint. The cohobated portions were distinctly reddish in color.

The second sample was baled before it became thoroughly dried and some fermentation set in before drying was completed after opening the bales. The leaves had turned brown and almost black, and an overwhelming odor of thymoquinone developed in the mass. The chief foreign material in this was sandburs.

*Monarda fistulosa*, 1918.—A quantity of oil amounting to 1715 Gm. was obtained from plants overmature, distilled August 23 and 24. When examined one crop of crystals had been removed from this oil and another was forming. It was of a very pale yellowish color, bright and clear, and was the lightest oil examined among those from the two crops.

Another oil had been obtained from plants fully mature, distilled somewhat earlier, August 8. The quantity obtained was 237 grammes in 0.32 percent yield. It was very dark brown and the red color was almost entirely lacking in this oil. It was free from any deposit.

From long dried and ripe flower heads 58 Cc. of oil were obtained having a reddish brown color.

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*Monarda fistulosa*, 1919.—The material was collected at various stages of development from early flowering to complete flowering and was divided into two lots. One had been freed from all foreign material such as weeds, grass and dead stalks; while the other portion had not been sorted in this manner. Both lots were distilled after drying and the aqueous distillate cohobated repeatedly until reduced to a small volume. These cohobated oils were collected separately and the density determined, and assayed.

These oils were of a reddish brown color, bright and clear. That from the sorted material is designated "cleaned" and was used for extraction of phenols from alkaline solution with ether in the attempt to isolate the methoxyl constituents present in these oils.

The results on these oils are shown in tabular form:

OILS OF <i>Monarda Punctata</i> .				
Date.	Description of material.	D <sub>20</sub> <sup>o</sup> Westphal.	Phenols. Dilute KOH (5 p. c.).	Remarks.
8-25-18	Leaves and stems	0.947	62.5 p. c.—heptane equal vol.	Crystalline layer, crystals from heptane.
1918	Ripe and dry flower heads	0.937	53.0 p. c.—heptane equal vol.	Crystals from heptane.
Florida var. from garden 10-15-19	Plant green and in full flower	0.9149	46.7 p. c.—oil direct	Yield direct 0.1055 p. c., cohobated 0.1574.
	1st cohobation	0.9668	88.9 p. c.—10 Cc. oil, 2 Cc. heptane	.....
	2nd and 3rd cohobation	0.971	94.2 p. c.—10 Cc. oil, 2 Cc. heptane	.....
Highlands Sample	Dried herb	0.9212	60.0 p. c.—oil direct	GREEN DRY Yield:
	1st cohobation	0.970	91.8 p. c.—10 Cc. oil, 2 Cc. heptane	0.645 p. c. 2.496 p. c. Cohob.: 0.684 p. c. 2.707 p. c.
Lone Rock "Baled"	Mixed with grass	0.9246	.....	Yield dry original, 0.8275 p. c.
	1st cohobation	0.9714	89.4 p. c.—10 Cc. oil, 2 Cc. heptane	Yield dry cohobated, 0.9479 p. c.
	2nd and 3rd cohobation	0.9750	95.4 p. c.—10 Cc. oil, 2 Cc. heptane	.....
Lone Rock "Fermented"	Entire plant	0.9295	56.6 p. c.—oil direct	Yield dry original, 2.101 p. c. Yield cohobated, 2.346 p. c. This material had fermented.
	1st cohobation	0.9677	87.2 p. c.—10 Cc. oil, 2 Cc. heptane	.....
	2nd and 3rd cohobation	0.9747	95.7 p. c.—10 Cc. oil, 2 Cc. heptane	Density of another lot of the original oil, 0.9305.

OILS OF <i>Monarda Fistulosa</i> .				
Date.	Description of material.	D <sub>20</sub> <sup>o</sup> Westphal.	Phenols. Dilute KOH (5 p. c.).	Remarks.
8-23-18	Over-mature plants	0.916	45.25 p. c.	2nd crop crystals in oil cryst. from heptane.
8-18-18	Mature plants	0.924	44.5 p. c.—heptane equal vol.	No crystals in oil, or from heptane. Yield of oil 0.32 p. c.

1918	Dry and ripe flower heads	0.952	44.0 p. c.—heptane equal vol.	No crystals in oil, or from heptane.
1919	Entire plant	0.9402	64.0 p. c.—oil direct	Yield original, 1.638 p. c.
	Cleaned material		62.0 p. c.	(dry) cohob., 1.859 p. c.
	1st cohobation	0.9700	90.2 p. c.—oil direct	.....
			89.6 p. c.	.....
	2nd cohobation	0.9755	96.0 p. c.—heptane	.....
			95.4 p. c. added afterwards	.....
	3rd and 4th cohobation.	0.9768	95.4 p. c.—5 Cc. oil	.....
			95.6 p. c.	.....
1919	Entire plant	0.9396	72.4 p. c.—10 Cc. oil, 5 Cc. heptane	Yield, original dry 1.724 p. c.
	Residual material		71.2 p. c.	.....
	1st cohobation	0.9750	90.0 p. c.—oil direct	Cohobated, dry 1.947 p. c.
			89.6 p. c.	.....
	2nd cohobation	0.9763	98.5 p. c.—10 Cc. oil, 2 Cc. heptane	.....
			98.5 p. c.	.....
	3rd and 4th cohobation	0.9770	98.2 p. c.—10 Cc. oil, 2 Cc. heptane	.....
			97.9 p. c.	.....

*Cohobation of Aqueous Distillates.*—The distillates resulting after the separation of the oily layer had been discarded, usually, but it is apparent that it contains almost all of the more readily soluble constituents of the oil and represents a saturated aqueous solution of whatever appears in the oil. Since the solubility of some of the oxygenated constituents of volatile oils in water is not insignificant, an attempt was made to recover them by redistilling repeatedly the aqueous distillates obtained from the herb. Where large quantities of herb are distilled this represents a large volume of water amounting to about a liter per kilo of dry herb. In every case about a third of the water was distilled over and the oil thus obtained separated. Of this distillate a third again distilled over until the volume became manageable. The oil only was examined from these cohobations. The first cohobated oil naturally contained the oil that had been incompletely separated from the first distillation and may be considered as a true cohobated oil contaminated with more or less of the original oil. The succeeding portions of oil were more carefully separated and represent more truly the nature of the portion of the oil soluble in water. Possibly the most soluble constituents of these oils are these phenols. Hence density determinations and assay indicated that the latter oils are practically pure phenol.

Thus, for instance, the yield of oil from green and fresh *M. punctata* in full bloom (Florida variety) was increased by one-half by cohobating the distillates three times.

Original oil.....	112.5 Gm.	0.1055 p. c.
Cohobated oil.....	55.3 Gm.	0.0519 p. c.
	167.8 Gm.	0.1574 p. c.
Total oil.....		

On a dried sample the difference was not so great and amounted to only about 10 to 15 percent of the original oil. Because of the high phenol content of the cohobated oils, their color is always distinctly reddish and some of the *punctata* cohobates could be readily induced to solidify.

With *M. fistulosa* much the same results were obtained and the yield of oil was increased about 15 percent on dried material.

A study of the tables of specific gravity and phenol assay indicates that the oils recovered by cohobation are almost pure phenols and that while the recovery of oil may be 15 percent or so, the recovery of phenols may amount to from 25 to 35 percent, a factor of some significance for these oils.

	<i>M. punctata.</i>		<i>M. fistulosa.</i>	
	Density.	Assay.	Density.	Assay.
Original oil.....	0.9295	56.6 p. c.	0.9396	71.8 p. c.
1st cohobation.....	0.9677	87.5 p. c.	0.9750	89.8 p. c.
2nd and 3rd cohobation.....	0.9747	95.7 p. c.	.....	.....
2nd cohobation.....	.....	.....	0.9763	98.5 p. c.
3rd and 4th cohobation.....	.....	.....	0.9770	98.1 p. c.
The phenols.....	0.977	.....	0.9777	.....

Oil sample,	<i>Monarda punctata.</i>			
	Direct.	1st cohob.	2d and 3d.	Total.
Florida variety.....	112.5 Gm.	38.0 Gm.	17.3 Gm.	167.8 Gm.
Highlands.....	278.0 Gm.	17.0 Gm.	6.5 Gm.	301.5 Gm.
Baled.....	965.0 Gm.	94.0 Gm.	46.0 Gm.	1105.0 Gm.
Fermented.....	1614.0 Gm.	142.0 Gm.	43.0 Gm.	1799.0 Gm.

Sample.	<i>Monarda fistulosa.</i>				
	Direct.	1st cohob.	2d cohob.	3d and 4th cohob.	Total.
"Cleaned".....	1865 Gm.	170 Gm.	54 Gm.	27 Gm.	2116 Gm.
Residual.....	3010 Gm.	259 Gm.	90 Gm.	44 Gm.	3403 Gm.

*The Heptane Test.*—The dilution of *Monarda* oils with heptane is frequently followed by the deposition of crystals of hydrothymoquinone and it was felt that a development of this test might lead to its establishment as of practical value for these oils. Frequently oils of *M. fistulosa* deposit crystals of hydrothymoquinone and an oil of *M. punctata* is found to do this occasionally. When, however, the oil is diluted with an equal volume of heptane a clear solution is not obtained, but the turbidity changes after hours to a crystalline deposit in almost every case. Of course, water may cause a similar turbidity. With oil of *M. fistulosa* exposure to cold has very slight effect on the amount or nature of the deposit, but with oils of *M. punctata* where hydrothymoquinone does not form so frequently as with the other oils, exposure to low temperature ( $-25^{\circ}$  C.) results in the deposition of thymol in rhombic crystals with characteristic markings.

The test was applied to all of the oils examined for 1918 and 1919. The original oils of *M. punctata* for 1918 were treated with an equal volume of heptane in small quantity, about 5 Cc. The oil "8-25" had already deposited a layer of crystals and more formed in heptane; while the other oil deposited crystals only in heptane. None of the 1919 oils could be induced to deposit crystals except at reduced temperature when thymol came out.

The oils of *M. fistulosa* not infrequently deposit the crystals readily in the oil, and almost invariably on dilution with heptane. However, one of the 1918 oils from the mature flower heads, containing only about 44 percent phenols, gave only an opalescence on the glass and no crystals formed. All of the other oils examined gave deposits. The cohobates of the oil designated "cleaned" were subjected to this test also. The original oil gave crystals at dilution of one volume, and an additional precipitate at a dilution with two volumes of heptane

At one volume none of the three cohobates deposited any crystals at ordinary temperature but at two volumes the second cohobate was induced to deposit a few; though in every case a turbidity resulted on the first dilution, which increased with the second dilution.

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#### A MORE PRACTICAL ASSAY PROCESS FOR SOME U. S. P. ZINC SALTS.\*

BY GEO. E. ÉWE AND FRED GLOOR.

The burdens of this communication are to emphasize the impracticability of the sulphide method of determining zinc in some U. S. P. zinc salts and to suggest the substitution therefor of the more practical ferrocyanide titration method.

The difficulties surrounding the application of the sulphide method are familiar to every analyst. The chief difficulties are the lack of assurance that the precipitation is complete, the necessity of allowing the precipitate of zinc sulphide to stand with warming for at least eighteen hours in order to complete the precipitation and obtain the precipitate in a sufficiently coagulated form to permit it to be collected on the filter and, most exasperating of all, the difficulty of properly washing the precipitate after it has been collected on the filter. The precipitate is usually so slimy that it is only with the exercise of the most extreme patience that proper washing can be effected at all. In addition to these difficulties, there remain the non-assurance that the treatment of the sulphide with nitric acid is really dissolving out all of the zinc (and that it is not being occluded by the clumps of sulphur formed by the reaction) and the persistence of some of the finely divided sulphur in passing through the filter with the possible production of varying small proportions of sulphate or sulphide in the weighed zinc oxide.

The accuracy of the sulphide method is above question where precise results are required and the proper precautions are observed to obtain these results, but where practical results are desired in a minimum of time the ferrocyanide titration method is infinitely superior.

The U. S. P. zinc salts which are now directed to be assayed by the sulphide method and to the assay of which the ferrocyanide titration method is applicable are the acetate, phenolsulphonate, sulphate and valerate. In addition, it is preferable to assay the chloride and the metal by this method.

The details of the ferrocyanide titration method, as found practicable in this laboratory, are as follows:

*Standard Solution Potassium Ferrocyanide.*—Dissolve 40 Gm., roughly weighed, of potassium ferrocyanide in enough distilled water to obtain a yield of 1000 Cc. Mix well and standardize as follows: Weigh accurately about 0.3 Gm. of chemically pure metallic zinc; place the weighed zinc in a beaker; dissolve it in 10 Cc. of U. S. P. hydrochloric acid; add about 100 Cc. of distilled water; neutralize with ammonium hydroxide; make barely acid with U. S. P. hydrochloric acid and add about 3 Cc. excess of the acid; add 10 Cc. saturated solution of ammonium chloride; heat nearly to boiling and titrate with the standard solution of potassium ferrocyanide, using a 5% solution of uranium acetate or nitrate acidified with

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