SCIENTIFIC SECTION

PHYTOCHEMICAL NOTES.

BY EDWARD KREMERS.

No. 107. A SURVEY OF THE INORGANIC CONSTITUENTS OF THE SEVERAL PARTS OF *Monarda fistulosa.**

BY ARTHUR A. HARWOOD.

While a study of the several constituents of the leaves, more particularly of the non-volatile constituents, was in progress a general survey of the various parts of the plant seemed desirable. This was especially true of the inorganic constituents which play an important rôle in the pigmentation of the plant. The results of this survey are herewith recorded.

The Root.—The moisture content of the air-dried material was found to be 4 p. c. (two samples) as determined by the xylene method. The same material yielded the following amounts of ash in two determinations:

	I.	II.
Water-soluble ash	1.19 p. c.	1.08 p. c.
Water-insoluble ash	10.17 p. c.	10.96 p. c.
Total ash	11.36 p. c.	12.04 p. c.

The water-insoluble ash resolved itself into:

Acid-soluble ash	2.99 p. c.	3.09 p. c.
Acid-insoluble ash	7.18 p. c.	7.87 p. c.

Upon analysis, the ash was found to contain the following elements and groups, the percentage, as above, being computed with reference to the air-dried material from which the ash had been obtained:

	Per cent.	Per cent.
Ca	0.34	0.34
Mg	0.071	0.071
Fe	0.19	0.18
Al	0.19	0.19
Cl	0.32	0.26
CO_3	0.025	0.024
SO_4	0.15	0.13
SiO_3	9.16	10.04
Undetermined	0.92	0.70

The Stem.—The moisture content of the air-dried material, as determined by the xylene method was found to be 6.60 p. c. and 6.40 p. c., respectively.

Two ash determinations yielded the following results:

	I.	II.
Water-soluble ash	2.62 p. c.	2.57 p. c.
Water-insoluble ash	1.45 p. c.	1.42 p. c.
Total ash	4.07 p. c.	3.99 p. c.

* Part of a thesis submitted for the degree of Doctor of Philosophy, University of Wisconsin. See also THIS JOURNAL, Vol. 18, page 228 and Vol. 19, page 1171; also Vol. 20, pages 17, 433 and 631.

The water-insoluble ash was constituted as follows:

Acid-soluble ash	1.41 p. c.	1.38 p. c.
Acid-insoluble ash	0.04 p. c.	0.04 p. c.

The following ash constituents were determined quantitatively:

	Per cent.	Per cent.
Ca	0.19	0.18
Mg	0.017	0.017
Fe	0.046	0.047
Al	0.049	0.047
Cl	0.028	0.028
CO_3	0.84	0.84
SO_4	0.16	0.16
SiO_3	0.79	0.83
Undetermined	1.95	1.84

The Leaf.—Two moisture determinations of the air-dried material yielded 7.40 p. c. and 7.20 p. c., respectively.

Ash determinations yielded the following results:

	I.	II.
Water-soluble ash	4.22 p. c.	3.87 p. c.
Water-insoluble ash	5.85 p. c.	5.66 p. c.
Total ash	10.07 p. c.	9.53 p. c.

The water-insoluble ash resolved itself into:

Acid-soluble ash	4.52 p. c.	4.67 p. c.
Acid-insoluble ash	1.33 p. c.	0.99 p. c.

The following constituents of the ash are computed with reference to the air-dried material:

	Per cent.	Per cent.
Mg	0.11	0.11
Ca	0.70	0.72
Fe	0.088	0.088
Al	0.18	0.16
Cl	0.035	0.025
CO_3	1.34	1.35
SO_4	0.63	0.69
SiO_3	1.74	1.35
Undetermined	5.25	5.04

The Bract.—The moisture content of the air-dried material as determined by the xylene method, was found to be 6.00 p. c. on two samples.

It yielded the following amounts of ash in two determinations:

	I.	II.
Water-soluble ash	5.24 p. c.	4.92 p. c.
Water-insoluble ash	7.31 p. c.	7.55 p. c.
Total ash	12.55 p. c.	12.47 p. c.

The water-insoluble ash resolved itself into:

Acid-soluble ash	4.23 p. c.	4.37 p. c.
Acid-insoluble ash	3.08 p. c.	3.18 p. c.

The quantitative analysis of the ash yielded the following percentages computed with reference to the air-dried material:

	Per cent.	Per cent.
Mg	0.11	0.11
Ca	0.59	0.58
Fe	0.10	0.10
Al	0.14	0.14
Cl	0.073	0.073
CO_3	1.40	1.40
SO_4	0.50	0.50
SiO_3	3.91	4.09
Undetermined	5.73	5.48

The Corolla.—Two determinations of the moisture content by the xylene method yielded 3.00 p. c. on both samples.

The following amounts of ash were obtained on two samples of the air-dried material:

	I. Per cent.	II. Per cent.
Water-soluble ash	4.66	4.64
Water-insoluble ash	2.81	2.81
Total ash	7.47	7.45

The water-insoluble ash resolved itself into:

Acid-soluble ash	1.75	1.84
Acid-insoluble ash	1.06	0.97

The following constituents were determined quantitatively, computed with reference to the air-dried material:

	Per cent.	Per cent.
Mg	0.061	0.059
Ca	0.32	0.31
Fe	0.088	0.088
Al	0.32	0.32
Cl	0.025	0.009
CO_3	1.73	1.73
SO_4	0.18	0.18
SiO_3	1.25	1.36
Undetermined	3.50	3.39

In the analysis of the ash constituents the following methods were employed:

Water-Soluble Ash.—For carbonates. The CO_3 content was determined by titration with $N/10$ hydrochloric acid, using methyl orange as an indicator.

For sulphates. The solution remaining after the carbonate determination was acidified with hydrochloric acid and barium chloride added until no further precipitation resulted. The barium sulphate thus formed was filtered, ignited and weighed and the SO_3 content computed from this result.

For chlorides. A sample of the water-soluble ash was acidified with nitric acid and an excess of $N/10$ silver nitrate solution added. The resultant silver chloride was filtered off and the excess silver nitrate determined by titration with $N/10$ potassium thiocyanate using ferric alum solution as an indicator.

Acid-Soluble Ash.—For iron and aluminum. The hydroxides of iron and aluminum were precipitated with ammonia as described by Treadwell.[1] The com-

[1] Treadwell and Hall, *Analytical Chem.*, Vol. II (1924), 110.

bined oxides of iron and aluminum resulting from the ignition of the hydroxides were dissolved in hydrochloric acid and the iron determined by the method of Zimmerman and Reinhardt.[1] The percentage of alumina was then determined by difference.

For calcium oxide. The filtrate from the iron and aluminum determinations was treated with oxalic acid and ammonium oxalate solutions as described in Treadwell's text.[2] The precipitated calcium oxalate was then collected on a filter and ignited and weighed as calcium oxide.

For magnesium oxide. The filtrate from the calcium oxide determination was treated according to the method of Schmitz as described by Treadwell.[3] The precipitated magnesium ammonium phosphate was ignited and the magnesium oxide calculated.

For silicic acid. The silicic acid present as the soluble salts of iron and aluminum was determined by evaporating the hydrochloric acid solution of the acid-soluble ash to dryness three times, finally filtering the desiccated silica, igniting and weighing.

Acid-Insoluble Ash.—For iron and aluminum. As small amounts of iron and aluminum frequently remain in the insoluble form as acid-insoluble ash, it was necessary to make a determination for the purpose of minimizing the error. The acid-insoluble ash was boiled with concentrated hydrochloric acid three times, the acid being evaporated each time. The filtrate was then treated as described above, the iron content being determined by titration with potassium permanganate solution and the amount of alumina obtained by difference. The percentages of iron and aluminum were then combined with the percentages obtained above to give the total result with reference to the air-dried material.

For silicic acid anhydride. The residue after treatment with concentrated hydrochloric acid was treated with sulphuric acid and hydrofluoric acid as described by Treadwell.[4] The percentage of SiO_3 so obtained was combined with that obtained in the acid-soluble ash.

For the sake of ready comparison the results reported above, also those obtained from the analysis with selective solvents, are herewith tabulated:

	Root.	Stem.	Leaf.	Bract.	Flower.	Seed.
Moisture content	4.00 p. c.	6.5 p. c.	7.3 p. c.	6.3 p. c.	3.0 p. c.	3.6 p. c.

Ash Determination.—The values given are the averages of the two determinations previously reported.

	Root, per cent.	Stem, per cent.	Leaf, per cent.	Bract, per cent.	Corolla, per cent.
Water-soluble ash	1.14	2.59	4.04	5.08	4.65
Water-insoluble ash	10.56	1.44	5.76	7.43	2.81
Total ash	11.70	4.03	9.80	12.51	7.46
Acid-soluble ash	3.04	1.39	4.59	4.30	1.79
Acid-insoluble ash	7.53	0.04	1.16	3.13	1.03

Inorganic Constituents.—In the following part of this tabulation, the amounts of elements and radicles were recomputed with reference to the absolutely dry mate-

[1] Treadwell and Hall, *Analytical Chem.*, Vol. II (1924), 519.

[2] *Ibid.*, page 86.

[3] *Ibid.*, page 78.

[4] *L. c.*, page 416.

rial, for any conclusions that may be drawn from these figures should be directly comparable and not subject to correction by the differences in the moisture contents of the several air-dried materials. The values recorded are the average of the two determinations previously reported.

	Root.	Stem.	Leaf.	Bract.	Corolla.
Ca	0.35 p. c.	0.20 p. c.	0.77 p. c.	0.63 p. c.	0.33 p. c.
Mg	0.074 p. c.	0.018 p. c.	0.13 p. c.	0.12 p. c.	0.062 p. c.
Fe	0.19 p. c.	0.050 p. c.	0.095 p. c.	0.11 p. c.	0.092 p. c.
Al	0.20 p. c.	0.049 p. c.	0.18 p. c.	0.15 p. c.	0.33 p. c.
Cl	0.30 p. c.	0.029 p. c.	0.032 p. c.	0.077 p. c.	0.017 p. c.
CO_3	0.026 p. c.	0.89 p. c.	1.45 p. c.	1.49 p. c.	1.78 p. c.
SO_4	0.15 p. c.	0.17 p. c.	0.71 p. c.	0.54 p. c.	0.19 p. c.
SiO_3	10.00 p. c.	0.87 p. c.	1.67 p. c.	4.26 p. c.	1.35 p. c.
Undetermined	0.90 p. c.	2.03 p. c.	5.53 p. c.	5.93 p. c.	3.54 p. c.

THALLIUM POISONING IN MIGRATORY BIRDS.

BY JUSTUS C. WARD.*

Since its introduction into the United States about 1920, thallium has been used with marked success in the control of injurious rodents. In areas where other poisons have failed to reduce the damage caused to ranchers and orchardists by these pests, thallium has proved highly effective. Thallium-poisoned grain is tasteless and the action of the poison is slow and insidious. There are no prompt warning features to limit acceptance, and rodents in most cases eat the entire bait-spots. In short, thallium is useful as a follow-up poison, but it is not a specific, that is to say, it will kill anything that eats it. Of recent years, thallium has been condemned as being responsible for losses of valuable species of birds and mammals.

A former publication (1) had to do with one phase of this problem, and it was definitely proved that thallium was wrongly blamed for sheep losses in the San Luis Valley in Colorado. The present investigation arose from a regrettable loss of wild geese around Yosemite Lake, California, found by investigators in that state to have been caused by thallium. The geese met their death from eating barley poisoned with thallium, which had been exposed by private individuals for a purpose not yet known.

References found in the literature (3) (4) relative to the toxicity of thallium to ducks or geese give no definite information relative to the toxicity to these birds of baits put out for Ground-Squirrels. The present investigations were undertaken to obtain this information. They were divided into: (1) Determination of the minimum lethal doses of thallium by intraperitoneal injection and by feeding; (2) observation of typical thallium death; (3) post-mortem observations; and (4) spectroscopic and chemical analyses.

Since no Canada geese were obtainable, female mallard ducks were used in all tests.

I. M. L. D. Studies: A. Intraperitoneal Injections.

* Associate Pharmacologist, Control Methods Research U. S. Biological Survey.