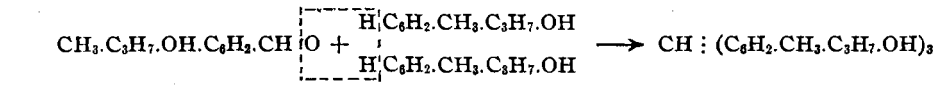

To use these reactions as a qualitative color test for either phenol appears to have been first suggested by Flueckiger[1] in 1888.

PHYTOCHEMICAL NOTES.*†

NO. 100. THE COROLLA OF MONARDA FISTULOSA L.

BY KARL H. RANG.

The corolla of this species has been subjected to chemical examination but once, *viz.* in 1903, and then only to a very partial and preliminary study.[1] Upon distillation, 340 Gm. of dried corollas yielded 9.24 Gm. or 2.71 p. c. of a dark reddish brown oil, the density of which (0.9586) indicated a high percentage of carvacrol and its oxidation products. Flueckiger's test gave a positive reaction for the monatomic phenol, the only substance indentified according to the report. The presence of quinhydrone, however, was assumed with little or no doubt. This assumption was later justified when quinhydrone crystals actually separated from the oil exposed to winter temperature. Upon keeping in a closed specimen bottle with cotton as a background for the blackish crystals, they changed color in the course of time. The thymoquinone part of the quinhydrone molecule apparently sublimed staining the cotton a light yellow, leaving the white crystals of hydrothymoquinone.[2]

In the summer of 1915 a considerable number of florets were collected and carefully garbled, but unfortunately no one was found to work with this valuable material.

During the summer of 1924 as much as 498 Gm. of dry florets were collected, for the most part about Madison. This material was used in the following experiments.

Moisture Determination.—The xylene method[3] was employed using a sufficient amount of hydrocarbon (250 cc.) to leave in the distilling flask enough solvent to cover the florets after all of the moisture had been driven over. Ten-Gm. samples of fresh florets, pickled in xylene as rapidly as the material was collected, yielded 7.5 cc., 7.8 cc. and 7.8 cc., respectively of water, hence 75 p. c., 78 p. c. and 78 p. c., respectively of moisture. This is appreciably higher than the moisture content of the corollas of *Monarda punctata* L. as found by Hewitt.

The air-dried material yielded 0.45 cc. of water in each of three experiments,

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[1] Flueckiger, "Pharm. Chemie," 2, 101.

* Scientific Section, A. PH. A., St. Louis meeting, 1927.

† From the laboratory of Edward Kremers.

[1] J. J. Beck, "Oil from the Corolla of Monarda Fistulosa," *Ph. Rev.*, 21, 111.

[2] Unpublished results.

[3] Bulletin No. 134, Forest Service. A. S. Dean, "The Estimation of Moisture in Creosoted Wood."

hence contains 4.5 p. c. of moisture. This is somewhat lower than the moisture content of the air-dried florets of *Monarda punctata* L. as found by Hewitt.

The distillation being ended, the xylene remaining in the flask was filtered while hot and the filtrate allowed to cool and to evaporate spontaneously. Upon cooling a few white crystals separated from each of the filtrates. The crystals from the combined and evaporated xylene filtrates, after recrystallization from water, melted at 235–237°. When heated, they charred thus revealing their organic nature.

The distillate was separated into its aqueous portion and into its hydrocarbon portion. Neither of the separated distillates, however, gave a test for carvacrol with Flueckiger's reagent.[1] That the xylene does not interfere with this test for thymol and carvacrol was established by experiment.

Ash Determination.—The air-dried florets were used.

I. 0.4992 Gm. of florets yielded 0.0123 Gm. of water-insoluble ash, 0.0405 Gm. of total ash, hence 0.0282 Gm. of water-soluble ash by difference.

II. 0.5000 Gm. of florets yielded 0.0142 Gm. of water-insoluble ash, 0.0404 Gm. of total ash, hence 0.0262 Gm. of water-soluble ash by difference.

III. 0.5007 Gm. of florets yielded 0.0140 Gm. of water-insoluble ash, 0.0408 Gm. of total ash, hence 0.026 Gm. of water-soluble ash by difference.

The percentages are herewith tabulated:

	I.	II.	III.
Total ash	8.11 p. c.	8.08 p. c.	8.10 p. c.
Water-insoluble ash	2.46 p. c.	2.84 p. c.	2.79 p. c.
Water-soluble ash	5.65 p. c.	5.24 p. c.	5.31 p. c.

Comparison with the ash content of the florets of *Monarda punctata* L. reveals that whereas the total ash content of those of *M. punctata* L. is about two per cent higher, the water-soluble ash content, however, is lower by one per cent and more. Taking into consideration the totally different types of soil on which these two species grow, *M. punctata* L. on sandy soil and *M. fistulosa* L. on clay soil, this difference may not be without significance.

Volatile Oil.—Four hundred and thirty-eight Gm. of air-dried florets were distilled with steam. The aqueous distillate was cohobated three times. The total oil, original oil plus that from the cohobations, amounted to 13.2 Gm. or 3.1 p. c. The original oil was of a deep red color, that from the first cohobation was a lighter red and the oils from the second and third cohobations were yellow with a red tinge thus revealing the lesser solubility of the pigments in water. The amounts, however, were by far too small in each case for separate investigation, hence the oils were mixed. The mixed oil was deep red in color. The density of the oil was 0.9740 at 23.3°. The specific gravity of this oil was higher than that of the oil distilled by J. J. Beck (1903)[2] *viz.* 0.9586. It is also higher than the specific gravity of the corolla oil of *M. punctata* L. distilled by Hewitt from corollas in 1924.

[1] Flueckiger's reagent consists of a piece of sodium hydroxide in chloroform. On addition of carvacrol or thymol a wine-red color is formed at the surface of the sodium hydroxide.

[2] *Ph. Rev.*, 21, 111.

The oils from three distillations being available they were diluted separately with heptane to precipitate any hydrothymoquinone present if possible. The ratios of oil to heptane were 1:1, 1:2 and 1:3, respectively. In no instance, however, was any hydrothymoquinone precipitated, even when more heptane was added and the solution exposed to the cold. While this does not show the absence of diatomic phenol, it indicates that but little hydrothymoquinone at most can be present.

The heptane solution of the third of these oils (8.8 cc. of oil in 26.4 cc. of heptane = 35.2 cc. of solution) was shaken with 5 p. c. aqueous KOH solution. 3.2 cc. of phenol were dissolved out by the aqueous alkali indicating a volume percentage of 36.3 p. c. of phenol. The heptane solutions of oils 1 and 2 combined (4.8 cc. of oil in 12.7 cc. of heptane = 17.5 cc. of solution) when treated in like manner gave up 1.7 cc. of phenol, corresponding to a volume percentage of 35.4 cc. These figures show considerable difference in the corolla oils examined.

From the aqueous phenylate solutions the phenols were regenerated. They were reddish brown in color. However, the amount of material was too small for satisfactory investigation.

The heptane solution of the non-phenols was heated to 100° to remove the solvent and the residue in the flask subjected to steam distillation. The resulting oil was likewise reddish brown in color and too small in amount for detailed investigation.

Both phenol and non-phenol portions were tested for thymol and carvacrol with Flueckiger's test. As was to be expected, the phenol portion gave a positive test, the non-phenol a negative test. A rough melting-point determination of the phenol made with a drop of oil suspended on a thermometer and frozen gave +1°, thus identifying it with carvacrol.

A color test[1] for monohydroxy thymoquinone gave a positive test with the phenol portion, a negative test with the non-phenol portion.

Like tests for dihydroxy thymoquinone gave negative indications in both cases.

Alcoholic Extract.—When extracted with hot alcohol, the corollas from which the oil had been distilled yielded a brownish red filtrate from which a flocculent precipitate separated upon cooling.[2] Evaporation of the alcohol yielded more, but the total amount was small. The substance melted at 139–141°. When burned it charred with intumescence.

The alcoholic filtrate from the corollas previously extracted with xylene (moisture determinations) was much lighter in color and upon cooling yielded no flocculent precipitate. However, upon evaporation such was obtained. It melted at 235–237°, but did not intumesce. It charred thus revealing its organic character.

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[1] A control test with monohydroxythymoquinone made by adding aqueous lead acetate to an alcoholic solution gave a red precipitate. See Wakeman, "The Higher Oxidation Products of Thymoquinone." Proc. A. PH. A., 58 (1910), 979.

[2] A control test with dihydroxythymoquinone made by adding aqueous lead acetate to an alcoholic solution thereof gave a green precipitate.