CONVERSION OF NITROSOCHLORIDES TO BENZYLAMINE AND PIPERIDENE BASES AND TO NITROSOPINENE.

The nitrosochloride obtained from fraction 153–163 was converted to nitrosopinene. (Heusler-Pond, p. 43.) The purified compound melted at 132° C. (m. p. of nitrosopinene = 132° C. Heusler-Pond).

From the nitrosochloride of fraction 163–168° the nitrolbenzylamine base was prepared, according to the method given in Heusler-Pond p. 43. It melted at 122° C. (m. p. of nitrolbenzylamine base of pinene = 122° C.).

The nitrosochloride of fraction 168–173° was converted to the nitrolpiperidide base. The pure compound melted at 118° C. (m. p. of nitrolpiperidide of pinene is 118–119° C.).

From the nitrosochloride of fraction 173–178° a nitrolbenzylamine base was prepared. It was found to melt rather low. The compound was recrystallized several times and was then found to melt rather sharply at 91–93° C. This melting point is far too low for the nitrolbenzylamine base of pinene. Moreover, the nitrolbenzylamine base of limonene melts at 93° C., which fact would seem to indicate that in fraction 173–178° limonene is present. However, no tetrabromide could be prepared from this fraction.

SUMMARY AND CONCLUSION.

A rather preliminary chemical investigation of the volatile oil of Canada balsam has been made. The presence of pinene, previously reported by Fluekiger has been confirmed. That there is at least one other terpene present in this oil is indicated by the boiling points of certain fractions and by the benzylamine base of fraction 173–178°.

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84. An Unusual Oil from Monardo Punctata.*

BY MAX PHILLIPS.†

In connection with the experiments on the cultivation of *Monardo punctata* it became necessary to collect a larger amount of seeds. Hence, between October 18 and 20, 1917, forty-five pounds of matured flower tops were collected. The corollas had dropped long ago, so that only the calyces with the mature fruit remained on the expanded base of the former influorescence. Having been stored for about a month, the fruit heads were threshed, 3.5 lbs. (= 7.7 percent) of seed being obtained. However, there also resulted 40 lbs. (18,181 Gm.) of chaff which was not devoid of odor. Hence, this material was subjected to steam distillation. The original oil (152 Gm.) and the cohobated oil (12 Gm.) were mixed, affording a total of 164 Gm. or 0.9 percent. This is an unusually high yield of oil for Monarda material collected so late in the season.[1]

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† Fritzsche Bros. Fellow.

[1] From the work that has been done upon *Monarda punctata*, it seems that the largest yield of oil is obtained from young plants not yet in blossom. Last November 800 lbs. of dry plants were distilled at this station and a 0.77 percent yield of oil was obtained. (See also N. Wakeman, "The Monardas," p. 24 of Univ. of Wis., *Bull.* 448.)

This oil was exceedingly dark in color, possessed the relatively high density of 0.952 and assayed 82 percent of phenol.[2] It may be that if the material had been distilled immediately after the seeds had matured, in late summer or early fall, the density would have been found lower and the phenol content not so high. Hence, the experiment should be repeated earlier in the season. Although the amount of oil obtained was small, it nevertheless invited at least a preliminary investigation. For this purpose it was roughly resolved into its phenol and non-phenol components by shaking out the former with aqueous 5 percent sodium hydroxide solution and recovering the phenols from the phenylates by means of acid. Previous exposure to so low a temperature as —22° C. for two days had not caused anything crystalline to separate, even though the oil was diluted with an equal volume of heptane.

Phenols.—It has already been pointed out that the phenol content of the oil was 82 percent. With so large an amount of phenol the assay with 5 percent aqueous potassium hydroxide was likely to cause minor difficulties of technique. As a matter of fact, two days did not suffice to effect a separation of the two layers. However, this was readily brought about by the addition of 5 cc. of heptane.

In the separation of the phenol from the bulk of the oil, 200 Cc. of 5 percent sodium hydroxide solution were used at a time until all of the phenol had been removed. The bulked aqueous alkaline solutions were shaken repeatedly with ether in order to remove non-phenols dissolved in the phenylate solution. After recovery of most of the ether, the remaining solution, upon exposure to the cold, crystallized to an orange-colored mass. The bulk of this residue (40 Gm.) consisted of thymol, as was shown, upon purification with petroleum ether, by both crystalline form and melting point. The purified pigment, however, looked more like dihydroxy thymoquinone than thymoquinone. Hence, in place of obtaining non-phenol materials, as expected, both substances isolated proved to be phenolic in character.

The aqueous phenylate solution was then rendered acid with hydrochloric acid, a dark brown, viscid oil separating. This was rectified by steam distillation and then by direct distillation, the operation being interrupted when the temperature of 235° had been reached. During the process of distillation, crystals were observed to form in the condenser. Recrystallized from water, they melted at 135 to 136° and, after further purification by sublimation, at 140°. They also gave Lieberman's[3] quinhydrone reaction with thymoquinone, hence may safely be pronounced as hydrothymoquinone. This diatomic phenol was also isolated from the "tarry" residue remaining in the flask from which the phenols had been distilled.

The phenol oil that had distilled over below 235° did not crystallize within a week, hence was fractionated. Most of it came over between 225 and 235° and this fraction crystallized after an hour's standing. The bulk of the crystals consisted of thymol, but again brick-red crystals of what looked like dihydroxy thymo-

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[2] The phenol content of the ordinary oil averages about 50 percent, though it runs as high as 60 percent. (See Wakeman's *Bull.* above given.) Hood even reports 72 percent, U. S. Dept. of Agr., *Bull.* 372.

[3] *Ber.*, 18, 3196.

quinone were observed. However, the amount was too small to make any tests of identity.

The aqueous distillate resulting from the steam distillation of the crude phenols was boiled with an excess of barium carbonate. The only observation worth recording was that the solution became wine colored, a color reaction produced by monohydroxythymoquinone under like circumstances

It may be worth while to point out that of the 45 Gm. of crude thymol separated in crystalline state from the oil, 40 Gm. were obtained from the ether[4] with which the alkaline phenylate solution had been shaken, and only 5 Gm. from the oily phenols separated from the aqueous phenylate solution by acid. Hence, of the 134 Gm. of phenol indicated by assay, only 45 Gm. or 33.5 percent crystallized out and were characterized as thymol. No small amount of phenol separated as "tar."

Non-Phenols.—The small amount of non-phenol portion of the oil was likewise fractionated. Below 177° only 10 Cc. came over, and between 177° and 235° less than 20 Cc. From the residue in the flask some hydrothymoquinone was separated as described under "phenols" and identified as such.

Conclusions.—Although the amount of oil was too small to accomplish much, nevertheless this preliminary investigation has added at least one substance to the list of known constituents of *Monarda punctata, viz.*, hydrothymoquinone.[5] Reasoning by analogy with *Monarda fistulosa*[6] seemed to show conclusively that it must be present in the plant, but its isolation had heretofore escaped all efforts. Moreover, the presence of monohydroxythymoquinone is indicated by a color reaction and that of dihydroxythymoquinone but wants definite chemical identification. Hence, this minor diversion from a major problem seems fully justified, and if only for the reason that it will stimulate the efforts to secure a much larger amount of material next year and thus take another step in further establishing the interesting parallel in the biochemistry of *Monarda punctata* and *M. fistulosa.*

COMMERCIAL CULTURES OF BULGARIAN BACILLUS.*

BY EDGAR B. CARTER.

A short historical sketch opens the paper to show that Metchnikoff did not originate the theory of the harmfulness of the absorption of bacterial toxins from the intestines nor was he the first to suggest the use of the Bulgarian Bacillus in the treatment of these conditions. The bacteriological characteristics and the chemical

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[4] The fact that thymol, dissolved in aqueous sodium hydroxide, can subsequently be shaken out with ether does not seem to have been reported in the literature before, although this phenomenon was observed by Jahns in connection with carvacrol. *Ber.*, 15, 817.

[5] It may be worth mentioning that hydrothymoquinone has been precipitated from ordinary, colorless, *Monarda punctata* oil by Dr. Edward Kremers by merely diluting the oil with the requisite amount of heptane; also that a number of previously unknown constituents have been isolated and identified by Dr. N. Wakeman. (See *Circulars of Wis. Pharm. Expt. Station.*) In both cases, however, the results had not been published at the time of this writing.

[6] I. W. Brandel, *Pharm. Rev.*, 19, 244.

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