against yeast. Neo-Silvol shows no inhibition of yeast growth at all, yet it has a germicidal value against *staphylococcus aureus* fully equal to Argyrol.

If the preparations are listed in order of their strength against the three tests, series will be obtained which will readily show that no direct relation exists between the inhibition of yeast growth and germicidal value.

The results of the Squibb Germicidal Test determinations are interesting in that they show some preparations to be very active within a short space of time, one minute, a point which should be of interest therapeutically. The phenol coefficient does not give this information.

From the results obtained the following conclusions are drawn:

The yeast test measures only the approximate silver-ion concentration and is of value only in distinguishing between "mild" and "strong" silver preparations. It is not absolutely reliable in distinguishing between preparations of the same group.

Silver-ion concentration is not directly related to the germicidal efficacy of colloidal silver preparations and consequently the yeast test cannot be used as an index to germicidal value.

In view of the cumbersomeness of the yeast test and the length of time required to perform it, it can well be replaced by the test recently developed by Keelan (7) in which an aqueous solution of the silver preparation is coagulated by exsiccated magnesium sulphate and the clear filtrate treated with hydrochloric acid. Strong preparations give a turbidity whereas mild preparations remain clear. This test requires very little apparatus and can be carried out in about five minutes.

I wish to express my appreciation to Dr. George F. Leonard of the New Brunswick Biological Laboratories, E. R. Squibb & Sons, for his determinations of the phenol coefficients and Squibb Germicidal Values reported herein.

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## THE VOLATILE OIL OF HYPERICUM PERFORATUM.*

BY EMERSON R. MILLER.

The genus hypericum contains about two hundred species belonging in the plant family *Hyperaceæ*, a group of beautiful flowering plants. A number of these species are mildly medicinal and some have been extensively used.

The species *perforatum* is commonly known as St. John's Wort. It is a native of Europe and Asia and was introduced into the United States as a garden flower.

* Read before Scientific Section, A. PH. A., Philadelphia meeting, 1926.

*Description and Range.*—This plant grows from one to two feet high and has numerous bright yellow flowers borne in dense terminal panicles. The flowers appear from June to August. Its range is from Maine to Wisconsin. It is said to be astringent, sedative and diuretic. It is used by Eclectic and Homeopathic physicians.

Analysis by Blair[1] shows that it contains volatile oil, resin, tannic acid and coloring matter. No further study of the volatile oil was made.

So far but one other reference to the volatile oil has been found in the literature. Haensel[2] reports a yield of 0.0928% of an oil having the following properties: $d_{20}$, 0.8703; optical rotation of a 50% solution in chloroform in 25-mm. tube, —1°10′; A. V., 23; S. V., 37.

*Experimental.*—In 1915 the writer collected a quantity of this plant for the purpose of making an investigation of the volatile oil. Seven samples of oil were obtained by steam distillation of material collected near Madison, Wisconsin. The material used was the whole plant above ground, collected from August 25th to September 9th. Many of the plants were still in bloom at the time of collection. Determination of the material was made by Prof. R. H. Denniston. The physical constants of the oils were determined soon after distillation. This part of the investigation, as well as the fractionation of the oil was carried out in the laboratory of plant chemistry of the University of Wisconsin.

In the following table are given the time of collection, percentage yield of oil and the physical properties of the different samples of oil obtained.

TABLE I.

| No. of sample. | Time of collection. | Percentage yield. | Specific gravity at 25°/15.6°. | Rotation in 100-mm. tube. | Index of Refraction. |
|---|---|---|---|---|---|
| 1 | Aug. 25 | 0.115 | 0.8095 | −16.0° | 1.4580 |
| 2 | Aug. 27 | 0.106 | 0.8065 | −12.4° | 1.4555 |
| 3 | Sept. 1 | 0.119 | 0.8155 | −19.6° | 1.4610 |
| 4 | Sept. 6 | 0.115 | 0.8140 | −17.9° | 1.4602 |
| 5 | Sept. 6 | 0.108 | 0.8180 | −17.8° | 1.4612 |
| 6 | Sept. 9 | 0.125 | 0.8125 | −14.9° | 1.4583 |

A small sample of the oil after standing about a year and a half in a completely filled bottle had undergone no appreciable change in color or odor. At this time the acid value was found to be 0.95, the saponification value, 6.88 and the saponification value of the acetylated oil, 25.07. With Schiff's reagent the oil gave no test for aldehydes. Agitation with 5% potassium hydroxide solution indicated the presence of a small amount of phenolic substance.

After determination of the physical properties of the oils all of the samples were united and kept in completely filled, well-stoppered bottles in a cool, dark place for several months. The oil was then subjected to fractional distillation three times, once under pressure of 55 mm. and twice under atmospheric pressure. In the following table are given the boiling temperatures under atmospheric pressure, also the density, the optical activity and the index of refraction of the several fractions of the oil.

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[1] *American Journal of Pharmacy*, 2, 23.

[2] Haensel, *Apotheker Zeitung*, 20, 45 (1905).

TABLE II.

| Number of fraction. | Boiling temperature. | Number of cc. in each fraction. | Density at 25°/25° | Rotation in 100-mm. tube. | Index of refraction at 20°. |
|---|---|---|---|---|---|
| 1 | Below 145° | 12 | 0.7506 | +4.6° | 1.4200 |
| 2 | 145–150° | 60 | 0.7580 | +5.5° | 1.4250 |
| 3 | 150–155° | 45 | 0.7875 | +6.0° | 1.4400 |
| 4 | 155–160° | 30 | 0.8105 | +4.1° | 1.4520 |
| 5 | 160–170° | 15 | 0.8210 | −1.4° | 1.4590 |
| 6 | 170–180° | 5 | 0.8235 | −4.3° | 1.4600 |
| 7 | Residue I | 6 | 0.9220 | −50.5° | 1.4990 |
| 8 | Residue II | 63 | 0.9093 | −4.0° | 1.4930 |

Residue I was the portion remaining after the distillation under diminished pressure. Residue II resulted from the fractionation under atmospheric pressure. Neither residue was examined further than to determine the physical properties as shown in the above table. Judging from the specific gravity and optical rotation these residues probably consisted largely of sesquiterpene. As will be seen by reference to the table Residue II shows a marked decrease in specific gravity and optical rotation as compared with the corresponding values for Residue I. This is most likely due to decomposition occurring during fractionation under atmospheric pressure, though it may be due in part to a difference in the concentration of certain constituents of the oil.

None of the properties of the fresh oil had suggested the presence of alpha pinene; but after standing several years, in completely filled, well-stoppered vials, kept in the dark, the lower boiling fractions had acquired the terebinthinate odor characteristic of pinene-containing oils which have stood for some time. Otherwise there was no appreciable change except in the color of the higher boiling fractions, some of which had become reddish brown.

*Identification of Alpha Pinene.*—The first two fractions were united and treated by the method of Wallach for the preparation of pinene nitrosyl chloride. Fractions 3, 4 and 5 were treated separately in the same manner. The following amounts of crude nitrosyl chloride were obtained from the respective fractions, with melting points as shown:

| Fractions. | Grams. | Melting point. |
|---|---|---|
| 1 and 2 | 2.444 | 100–101° |
| 3 | 2.435 | 97–99° |
| 4 | 1.925 | 93–94° |
| 5 | 0.469 | 93–95° |

The nitrosyl chlorides were purified three times by dissolving in chloroform and precipitating by the addition of methyl alcohol. After pressing between filter paper and standing in a vacuum dessicator over sulphuric acid the melting point of the compound obtained from Fractions 1 and 2 was 101–102°, but that of the other fractions still remained a few degrees lower than that generally given for pinene nitrosyl chloride, namely 103–104°. From the purest of the nitrosyl chlorides a nitrol piperidide was prepared having the melting point 118°. These results show that alpha pinene of low dextrorotatory power is a constituent of the oil.

PROBABLE PRESENCE OF AN ALIPHATIC HYDROCARBON.

The boiling temperature, density and index of refraction of the first two fractions show conclusively that quite an appreciable amount of some compound or compounds other than alpha pinene is contained in the oil.

The filtrates from the preparation of the nitrosyl chlorides were separately mixed with a relatively large volume of water, whereupon three distinct layers were formed. The lower layer was thick and highly colored. This was not further examined. The upper layer was thoroughly washed with distilled water until free from acid, dried over anhydrous calcium chloride and then distilled. The temperature rose rapidly to 140° and most of the liquid came over at 140–142°. The specific gravity at 20° was 0.7135, the index of refraction at 18.8°, 1.4048 and the optical activity practically 0°.

This low boiling oil was then allowed to stand in contact with concentrated sulphuric acid for several days with frequent agitation. The acid layer became colored reddish brown. This treatment was repeated until the sulphuric acid ceased to show coloration. Only a very slight diminution in the volume of the oil occurred by this treatment. The oil thus purified was then distilled and was found to pass over almost completely at 140–142°, uncorrected. Following this it was boiled a short time with concentrated nitric acid with no apparent change since it again distilled almost entirely at 140–142°. This fraction of the oil is most probably an aliphatic hydrocarbon not hitherto known to occur in a volatile oil.

Among the paraffins and cycloparaffins several hydrocarbons are known having physical constants similar to those of this fraction of the oil of hypericum.

Among such compounds are the following:

1-2-4-trimethyl cyclohexane, b. p., 140°; d. 0.778; $n_D$, 1.429.
1-1-3-trimethyl cyclohexane, b. p., 138°; d. 0.790; $n_D$, 1.436.
1-3-5-trimethyl cyclohexane, b. p., 138°; d. 0.772; $n_D$, 1.429.
2-6-dimethyl octane, b. p., 159°; $d_4^{20}$, 0.7313; $n_D$, 1.411.
4-methyl octane, b. p., 141.7–141.9°; $d_{15}^{15}$, 0.7320; $n_D$, 1.4027, at 25°.
3-ethyl hexane, b. p., 118.8–119°; $d_{15}^{15}$, 0.7175; $n_D$, 1.3993, at 25°.
Fraction of oil of Hypericum, b. p., 140–142°; $d_{20}^{20}$, 0.7135; $n_D$, 1.4048, at 18.8°.
$\alpha_D$, 0°.

The molecular weight of this fraction of oil was found to be approximately 133. Mr. E. F. Williams is due credit on the molecular weight determinations.

*Summary.*—The average yield of oil was 0.1146%.

Average values for six samples of oil were as follows:

$d_{15.6}^{25}$, 0.8126; $\alpha_D$, −16.43°; $n_D$ (20°), 1.45903.

There has been identified alpha pinene, which forms a considerable part of the oil. The physical properties of the high boiling fractions make it reasonably certain that the oil contains one or more sesquiterpenes.

The oil is of unusual interest because of its low boiling temperature, its low density and its low index of refraction.

The lowest boiling fraction of the oil had the following characteristics:

B. p. 140–142° (uncor.); $d_{20}^{20}$, 0.7135; $n_D$, 18.8°, 1.4048.

In several respects this fraction shows the behavior of an aliphatic hydrocarbon.

## MONARDELLA OIL.

BY EMERSON R. MILLER.

Several years ago while spending a summer in California the writer observed that a species of *Monardella* grew abundantly in several localities, particularly in the Yosemite and in the Lake Tahoe region.

According to the descriptions given in Hall's "A Yosemite Flora" the species in question is probably *Monardella lanceolata* Gray, commonly known as Western Pennyroyal. The plant is of special interest on account of its odor which suggests the presence of pulegone.

A small quantity of this plant was collected and, in the air-dried condition, was steam distilled at Auburn, Aabama. The yield of oil was practically one per cent.

The physical constants of the oil were as follows:

$d_{15°}^{25°}$, 0.9392; $n_{D18°}$, 1.4908; $\alpha_D$, +17.4°

For identification of pulegone a semicarbazone was prepared from the oil, m. p. 167°. The oil also yielded an oxime (isopulegone oxime) m. p. 118–120.°

A comparison of the physical constants of the oil with those of pulegone would seem to show that the oil consists principally of pulegone.

| | Oil of Monardella. | | Pulegone. |
|---|---|---|---|
| $d_{15°}^{25°}$ | 0.9392 | $d_{15°}$ | 0.939 |
| $n_{D18°}$ | 1.4908 | $n_{D20°}$ | 1.488 |
| $\alpha_D$ | +17.4° | $\alpha_D$ | +20° to 23° |

The quantity of oil obtained was not sufficient for a further investigation.

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## USE OF THE MONESS AND GIESY VISCOSIMETER TO CHECK THE SAYBOLT UNIVERSAL VISCOSIMETER.

BY W. E. HONSINGER.

We desired to check the results obtained with the Saybolt Universal Viscosimeter at 100° F. on liquid petrolatum by using the instrument designed by Moness and Giesy and described in THIS JOURNAL. (1)

The viscosimeter was made and set up as described in that article. The rate of flow of a 37% by weight alcohol-water mixture of known viscosity (2) was measured with results ranging between 73 and 74 seconds. The radius of the capillary was found by making the proper substitutions in Bingham's equation (3) and solving for R. This result was checked by weighing the mercury thread and calculating the radius from this weight, the sp. gr. of mercury and the length of the capillary tube.

Three samples of liquid petrolatum from different lots were taken and their