

from ragweed, it also slowly becomes indistinctly crystalline on long standing in the desiccator, and slowly reduces Fehling's solution.

Conclusions.

In view of the uncertainty attending the accurate analysis of an amorphous body of this kind, we believe that the results obtained from the analysis of the bitter principle of common ragweed and of absinthin from wormwood justify us in concluding that the two bodies are probably identical. Other pharmacological studies tend to show that the use of preparations of ragweed in the treatment of hay fever is based on irrational grounds.

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THE VOLATILE OILS OF THE GENUS *SOLIDAGO*.

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The genus *Solidago* is represented in the United States by about seventy-five species. Some of these occur quite abundantly but can, as yet, scarcely be considered of any economic importance. A few have been used medicinally, particularly *Solidago virgaurea* Linn., which is common to Europe and North America, and *solidago odora* Ait., which was at one time recognized by the United States Pharmacopoeia. The root of *Solidago canadensis* L. is said to contain a coloring matter once used in Canada as a valuable dye.

Very little is known about the chemistry of the plants of this genus. Volatile oils have been obtained from four species, but with the exception of the oil of *Solidago canadensis* L. nothing is known about their chemical composition. According to Schimmel & Co.,¹ the constituents of the last named oil are *pinene* (85%), *phellandrene*, *dipentene*, *limonene*, *bornol* (9.2%), *bornyl acetate* (3.4%), and *cadinene*.

The Volatile Oil of *Solidago nemoralis*.

Solidago nemoralis Ait. is one of the smaller species of the genus, growing from Quebec to the North West Territory, south to Florida, and west to Texas and Arizona.

In their report of April-May, 1906, page 63, Schimmel & Co. give the following description of a sample of oil of *Solidago nemoralis* which they received from America: "The bright olive-green oil had a peculiar odor, reminding somewhat of cypress oil. The constants were: d_{15}° 0.8799, α_D $-23^{\circ} 10'$, ester number 14.4, ester number after acetylation 38.2. The oil formed a cloudy solution in about seven and more volumes of 95% alcohol."

¹ Report, April, 1894, p. 57.

The oil used in our investigation was prepared by steam distillation from the fresh herb (root excluded) collected, mainly, in the flowering stage during the month of October. Ten samples were obtained; the percentage yield and optical rotation in a 100 mm. tube were as follows:

| No. of sample. | Yield. Per cent. | Optical rotation. | No. of sample. | Yield Per cent. | Optical rotation. |
|----------------|------------------|-------------------|----------------|-----------------|-------------------|
| 1..... | 0.34 | -17.73° | 6..... | 0.31 | -14.82° |
| 2..... | ... | -16.92° | 7..... | 0.30 | -16.35° |
| 3..... | 0.24 | -16.60° | 8..... | 0.33 | -15.77° |
| 4..... | 0.316 | -16.64° | 9..... | 0.33 | -15.73° |
| 5..... | 0.43 | -15.73° | 10..... | 0.30 | -15.70° |

The average per cent yield was 0.322.

The investigation was carried out upon the mixture of these samples.

Physical and Chemical Properties of the Oil.

In color and odor the oil was similar to the sample described by Schimmel & Co., quoted above; but in other respects differed considerably from that oil, as is seen from the following data: d_{25}^{25} 0.8532; α_D -16.17°; n_D^{18} 1.47397. Soluble in about four volumes of 90% alcohol, in about 24 volumes of 70% alcohol. Saponification number, 5.6; after acetylation, 9.4.

Test for Phenols.—5 cc. of the oil were shaken in a cassia flask with an excess of 5% potassium hydroxide solution and enough water then added to bring the oil into the graduated neck of the flask. The diminution in volume was very slight, approximately 0.03 cc., corresponding to 0.6% of phenol. But the total amount of phenol subsequently separated from the oil was less than this.

Test for Ketones and Aldehydes.—With Schiff's reagent no coloration was produced within two minutes. With phenyl hydrazine only a very slight cloudiness was produced. The oil may, therefore, be said to be practically free from aldehydes and ketones.

Saponification and Fractionation of the Oil.—The total quantity of oil was shaken several times with a 3% solution of potassium hydroxide, and, after the aqueous alkaline liquid was separated as completely as possible, the oil was heated about three-quarters of an hour on a boiling water bath with an excess of 0.5 N alcoholic potassium hydroxide solution. The greater part of the alcohol was then distilled off on a water bath and the contents of the flask diluted with a large volume of water. The oil, which separated, was removed from the alkaline liquid, washed until free from alkali, dried with anhydrous sodium sulfate and subjected to fractional distillation under a pressure of 23 mm. The fractionation was carried out three times. Fractions having the following constants were obtained:

| Fraction. | Boiling temperature. | Rotation in 100 mm. tube. | Sp. gr. at $\frac{25^\circ}{25^\circ}$. |
|-----------|----------------------|---------------------------|--|
| 1..... | 57-59° | -19.5° | 0.8525 |
| 2..... | 59-61° | -13.28° | 0.8607 |
| 3..... | 61-72° | +7.86° | 0.8609 |
| 4..... | 72-80° | +45.87° | 0.8610 |
| 5..... | 80-100° | +43.46° | 0.8923 |
| 6..... | 100-120° | -12.83° | 0.9226 |
| 7..... | Residue | | |

Identification of Pinene.—Fractions No. 1 and 2 constituted the main portion of the oil. When distilled under diminished pressure the greater part of Fraction No. 1 boiled between 159° and 165°. From this distillate a nitrosyl chloride was prepared both by the method of Wallach¹ and that of Ehestaedt,² the melting point of the product being 102-103°. From the nitrosyl chloride a nitrol piperidide was prepared having the melting point 118-119°.

The alcoholic distillate recovered from the saponification mixture was diluted with a large volume of water. The oil which was thus thrown out of solution was separated, washed, dried, and found to have the following constants: B. p., 161-165°; α_D , -19.37°; d_{25}^{25} , 0.8523.

This liquid was also identified as pinene by the preparation of a nitrosyl chloride, m. p. 103°, and a nitrol piperidide, m. p. 118-119°.

A nitrosyl chloride was also prepared from Fraction No. 2, but the yield was smaller.

Examination for Phellandrene.—Fraction No. 3 was tested for phellandrene by Wallach's method for the preparation of phellandrene nitrosites but with negative results. Fraction No. 4 was tested in the same manner, but it also yielded no nitrosite.

Examination for Borneol.—Since the maximum boiling point of Fraction No. 5 is near that of borneol and the odor of this fraction was somewhat suggestive of that of borneol, an attempt was made to prepare borneol phenyl urethane by means of carbanil, but the results were negative. Fraction No. 6 was also treated in the same manner but likewise with negative results.

A further attempt to identify borneol was made as follows: the remainder of Fraction No. 5 and a part of Fraction No. 6 were mixed and distilled under ordinary pressure. The portion which came over between 195° and 220° was oxidized by means of chromic acid mixture, the acid liquid neutralized with sodium carbonate and then distilled with steam. There was no indication of the separation of camphor in the condenser, though the oily distillate had a somewhat camphoraceous odor. This oil was treated with hydroxylamine hydrochloride in order to see if camphor

¹ *Ann.*, 245, 251 (—).

² *Report of Schimmel & Co.*, April, 1910, p. 164.

oxime could be prepared. The thick, oily mass which was obtained had an odor very suggestive of camphor oxime and a few crystals had separated, but at the time of this writing the amount was insufficient for a melting point determination.

Examination for Camphor.—The remainder of Fraction No. 6 was treated with hydroxylamine hydrochloride but no oxime could be separated, indicating the absence of camphor.

Examination for Phenol.—Identification of Salicylic Acid. The aqueous alkaline liquid obtained by shaking the oil with 3% solution of potassium hydroxide was acidulated with dilute sulfuric acid, shaken out with ether and the ether allowed to evaporate. A thick, brownish red liquid was thus obtained from which, after standing some time, needle shaped crystals separated in very small amount. This substance gave an intensely violet color with aqueous ferric chloride solution. When treated with methyl alcohol and sulfuric acid it gave the odor of methyl salicylate.

Identification of Acetic Acid.—The aqueous alkaline liquid resulting from the saponification of the oil was acidified with dilute sulfuric acid and the mixture subjected to steam distillation. From the acid distillate a silver salt was prepared which, on ignition, yielded 65.7% metallic silver. Silver acetate contains 64.64% of silver.

Summary.

The chief constituent of this oil is α -pinene, a mixture of the *dextro* and *levo* forms. In addition, it contains salicylic acid and acetic acid, at least one alcohol, occurring both in the free state and combined as the acetate. The presence of borneol is quite probable.

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NOTES.

A Modified Kjeldahl Flask for Determining Soil Nitrogen.—Soil chemistry and soil bacteriology call for the determination of soil nitrogen. The nitrogen content of ordinary soil is small and the sample has to be correspondingly large. The fact that most directions call for the transfer of the solution between digestion and distillation shows that the ordinary Kjeldahl flask is not adapted to this determination. Some investigators do not make it a rule to transfer, but they sometimes are forced to, since with some types of soil, such violent bumping occurs that the flask breaks. The transfer is a nuisance, involving extra time and flasks, besides allowing a source of error.

The modified Kjeldahl flask represented in the accompanying sketch does away with the bumping, making the transfer unnecessary. This flask holds about 700 cc. It has the same proportions as the ordinary