

carbonate was added in excess, the precipitate filtered off, the filtrate evaporated to a small bulk, again filtered, and allowed to evaporate to dryness over sodium hydroxide. Leaf-like crystals were deposited. These were dissolved in a small quantity of hot water, the solution filtered, and after the addition of a drop of dilute nitric acid, silver nitrate was added. This precipitated a salt which in a few seconds turned brown and then black. This mixture was heated, the black substance was filtered off, and upon chilling the filtrate, a white salt was obtained. This salt was unstable, turning dark upon standing. The salt was filtered off, dried on porous plate over sulphuric acid, and the silver determined as silver chloride.

0.1006 g. salt gave 0.0858 g. silver chloride.

Percentage of silver in salt=64.24.

Calculated for silver acetate=64.66.

The solution of the barium as well as of the silver salt in hot water had a distinct fatty acid odor, thus indicating the presence of at least traces of other acids.

PHYTOCHEMICAL NOTES.*

78. AN UNUSUAL OIL OF WORMWOOD.

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Several years ago there was left at the laboratory a sample of oil of wormwood by Mr. Leander Drew, the well-known wormwood distiller of Sauk Co., Wisconsin. For more than half a century wormwood has been cultivated and distilled in Sauk Co. by three generations of the Drew family. This sample of about a pound had been set aside by Mr. Drew because of its unusual density. Mr. Drew could not account for the peculiarity of the sample which in other respects resembled the general run of oil of the same still and season.

The specific gravity of the oil determined by means of a Mohr-Westphal balance at 21.5° was found to be 1.000. The usual density of wormwood oil is supposed to vary between 0.925 and 0.955¹

The saponification number was first ascertained in the usual manner by boiling about 2 grams with 20 cc. N/2 alcoholic potassium hydroxide solution for 40 minutes. Two determinations yielded 151 and 150 respectively as saponification numbers.

Owing to the dark color of the reaction mixture, the method of saponification was modified in a manner that has proven effective on previous occasions. About 5 grams of oil were heated with 50 cc. of N/2 alcoholic potassium hydroxide solution for 90 minutes. The saponification mixture was transferred to a 500 cc. measuring flask and diluted with water so that the oil rose above the mark in the neck of the flask, thus yielding exactly 500 cc. of aqueous alkaline liquid. The reaction mixture thus diluted was next transferred to a separating funnel and the aqueous portion was drawn off through a filter. Of the filtrate, portions of 100 cc. were used for titration with standard acid. The dark oil being thus

*From the laboratory of Edward Kremers.

¹G. H. K., The volatile oils, p. 685.

removed from the aqueous alkaline reaction mixture, titration with standard acid became much easier. 181 and 182 respectively were the saponification numbers obtained in two separate experiments.

After this the bulk of the oil, 297 grams, were saponified by boiling for 1 hour with 120 grams of potassium hydroxide dissolved in alcohol. The mixture was then subjected to steam distillation. After the alcohol had distilled over, the oil was collected, the last portion of which was green.

Sulphuric acid was now added in slight excess to the alkaline residue and the steam distillation resumed. An aqueous acid distillate was thus obtained. From the residual water there separated upon cooling a large quantity of white crystals in addition to tar. More crystals were obtained from the tar itself by boiling with hot water, etc. The original crystals, purified by re-crystallization, melted at 146 to 152°; those obtained from the tar at 152-153°. The combined crystals, purified still farther by re-crystallizing twice from water, melted at 156°.

Melting point, solubility, color test with ferric chloride, and odor test when heated with sulphuric acid and methyl alcohol all point to salicylic acid. The exact amount of salicylic acid present was not ascertained. After the saponification, 160 grams of oil had been recovered and 70 grams of tar, leaving a difference of 67 grams, the greater portion of which probably was salicylic acid.

The aqueous distillate obtained from the steam distillation of the acidified saponification reaction mixture was neutralized with an excess of barium carbonate and the solution of barium salts evaporated. Organic acids present were precipitated in the usual manner as silver salts, the precipitation, however, being conducted fractionally. Of the silver precipitates thus obtained silver determinations were made with the following results:

(1.) 0.230 grams of the first precipitate yielded, on ignition, 0.170 of metallic silver, corresponding to 73.9 p. c. silver: Calculated for silver formate 70.6 p. c. silver.

(2.) 0.319 grams of the third precipitate yielded, on ignition, 0.141 grams of metallic silver, corresponding to 44.2 p. c. of silver. Calculated for silver salicylate 44.1 p. c.

Of the oil distilled over from the alkaline reaction mixture, 10 cc. were acetylated in the usual manner. The acetylated oil yielded upon saponification 229.7 and 234.8 respectively as saponification numbers.

The remainder of the oil, 150 grams, or about 168 cc., was fractionated, the bulk, 125 cc., distilling over between 145 and 200°. It had a specific gravity of 0.9127 at room temperature. Allowed to stand for 11 days with 50 cc. of alcohol and 125 cc. of a saturated solution of sodium bisulphite, 40 grams of crystals, presumably the thujone addition product were obtained. The remaining oil upon fractionation was collected in three fractions:

I—185 to 190°

II—190 to 195°

III—195 to 200°

At this point the study of this peculiar oil had to be broken off. Its principal interest lies in the unaccountable presence of salicylic acid. None of the other oils distilled semi-occasionally on the Drew farm is supposed to contain salicylic acid, neither are any of the weeds on the farm known to contain this acid.