

## THE DETECTION OF CAMPHOR OIL IN THE NATURAL OIL OF SASSAFRAS.

BY E. H. GRANT.\*

Sassafras oil is defined by the United States Pharmacopoeia IX as "A volatile oil distilled from the root of *Sassafras variifolium* (Salisbury) O. Kuntze (Fam. *Lauraceae*)."<sup>1</sup> It is used extensively as a flavor, being the basis of the so-called "sarsaparilla" flavors, as a mild antiseptic, as an ingredient of liniment and as a perfume, especially in cheap toilet soaps. The principal constituent of this oil is safrol, which is present to the extent of about 85 percent. When Schimmel & Co. showed the presence of safrol in camphor oil and developed methods for separating it in a fairly pure state, imitation oil of sassafras was soon an ordinary article of commerce and at present is used in much larger quantities than the natural oil of sassafras.

As by-products in the manufacture of camphor, there are obtained various waste camphor oils, varying much among themselves in specific gravity, color and composition. Certain of the darker oils rich in safrol are called "sassafrassy oils of camphor" and are used in the manufacture of imitation oil of sassafras. The safrol is frozen out and pressed. The residual oil is fractionated and certain fractions of suitable specific gravity are mixed with safrol to give a product very similar in composition to natural oil of sassafras.

The commercial synthetic oils, carefully made, have the same specific gravities as natural oils. Their optical rotation, however, is usually low, in the neighborhood of  $+1.75^\circ$  at  $25^\circ\text{C}$ ., whereas the U. S. P. limits are  $+3^\circ$  to  $+4^\circ$ . Since many natural oils polarize much below  $+3^\circ$ , the optical activity is not very valuable in detecting an adulterated or synthetic oil.

The reported constituents of sassafras oil are safrol, eugenol, pinene, phellandrene, *d*-camphor, sesquiterpenes and unidentified substances of high boiling points (Power and Kleber, *Pharm. Review*, 14, p. 101). Various chemists in reporting on camphor oil have shown it to be a very complex mixture and to contain, among other compounds, all of those mentioned as being present in sassafras oil. Schimmel & Co. report the chief phenolic body present to be eugenol, with traces of carvacrol. By the method outlined below, I have found that carvacrol is probably the predominating phenol in such waste camphor oils as are used for the manufacture of safrol. As I have not examined all varieties of camphor oil, however, I am not prepared to state that this is generally the case. Examination of five samples of "sassafrassy oils" obtained through the U. S. Customs Service from importations and of numerous commercial imitation sassafras oils showed that the bulk of the phenols is carvacrol, while eugenol is present in comparatively small amounts. Applying the same test to commercial safrol made from waste camphor oil showed it to contain traces of one or more other phenols whose identity was not determined.

The method used depends on the formation of various colored diazo dyes and is as follows:

---

\* Research Chemist, Wm. S. Merrell Co., Cincinnati, O. Work was performed while in charge of drug laboratory, New York Station, U. S. Bureau of Chemistry.

Dilute about 5 Cc. of the oil with about 20 Cc. of petroleum ether. Add 5 Cc. of water and 1 Cc. of 10% NaOH. Shake out the phenols, draw off the aqueous layer and acidify it. In another beaker put 5 Cc. of water, a few drops of 10%  $H_2SO_4$  and then 1 Cc. of a saturated alcoholic solution of paranitraniline. Add a 1% solution of  $NaNO_2$  drop by drop until the yellow color of the paranitraniline is almost destroyed. If, for any reason, the color is not destroyed evenly and quickly by the nitrite, this indicates that the diazotization is not proceeding correctly, and the solution must be discarded and a new lot diazotized with greater care. Add a small amount of dry urca to destroy the excess of nitrite. Pour the phenolic solution into the diazotized paranitraniline solution. Make alkaline with 10% NaOH and then just acid with dilute  $H_2SO_4$ . Extract with petroleum ether. Draw off the ethereal layer and free it from any solid particles of dye floating in it or adhering to the sides of the separatory funnel. Add about 20 Cc. of water and a few Cc. of 10% NaOH to the petroleum ether in a separatory funnel and shake. Draw off the alkaline layer and filter it through filter paper to free it from petroleum ether. Treat authentic samples of sassafras oil and synthetic sassafras oil from oil of camphor in the same way. Dilute the three solutions until the depth of color is practically the same in all, and is of a strength best suitable for comparison. The phenols from natural oil of sassafras give a purplish red color; those from waste camphor oil give an orange-red color; a mixture of these two gives an intermediate tint.

This method, while it gives a good idea of the relative proportions of the two oils in a mixture, is not suited, without modifications, for an exact quantitative determination. If ether is substituted for petroleum ether, the dye can be extracted quantitatively, but is not obtained in as pure a state in the final stage.

The phenols from sassafras oil give a dye identical in shade with that of the dye made from eugenol. The phenols from synthetic oil or waste camphor oil give dyes the same in shade as that made from carvacrol, except that the dyes from these oils tend slightly towards purple, indicating the presence of a trace of eugenol.

Five samples of sassafras oil were distilled in the laboratory from commercial samples of sassafras root bark from various parts of the United States. Generally the exact source was not known accurately, but one sample was collected especially for this work from western North Carolina. One sample of oil was distilled under constant supervision of members of the Bureau of Chemistry at a commercial plant in Junction City, Ky., from the whole sassafras roots and stumps ground up in the usual commercial manner. Examination of these oils and of many commercial samples of probable purity all yielded dyes of an identical shade.

Mr. E. K. Nelson, of Washington, D. C., has called my attention to the necessity of using pure paranitraniline in this test. He was unable to obtain satisfactory results with the commercial chemical, but did obtain good results later with a purer preparation. Another important point to be observed is to see that the diazotizing proceeds in an orderly manner so that excessive amounts of colored by-products are not obtained.

The author regrets that press of work and, later, his resignation from the Government service have prevented him from investigating this subject further.

---