[CONTRIBUTION FROM THE DIVISION OF FOODS OF THE BUREAU OF CHEMISTRY.]

THE DETECTION OF SMALL QUANTITIES OF TURPENTINE IN LEMON OIL.

BY E. M. CHACE.

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The method ordinarily used to detect the presence of turpentine in lemon oil is that offered by the laboratories of Schimmel and Company in 1896.[1] It depended upon the difference in rotation between the original oil and the first 10 per cent. distilled therefrom in a three-bulb Ladenburg flask. Pure oil distilled in this way, the authors say, should not show in the distillate a rotation of over 2° 57′ less than that of the original oil; whereas samples of mixtures of lemon oil, orange oil and turpentine showed a marked difference, amounting to 7° 17′ on a sample containing 90 per cent. lemon oil and 10 per cent. of a mixture of orange oil and turpentine, 71 per cent. of the former to 29 per cent. of the latter, thus containing but 3 per cent. turpentine.

Soldaini and Berte modified this method, distilling 50 per cent. in place of 10 per cent. This fraction should have a higher rotation than either the original oil or the residue. Both methods have been used with some success but both are open to several objections, the greater of which seems to be the discordant results obtained by different analysts working under different conditions. The size and shape of the flasks, the rate of distillation and many other factors affect materially the results obtained. Another objection is the variation in the rotation of turpentine. In the first method mentioned the sample of American turpentine used had an angular rotation at 20° of +6°. The Paper and Leather Laboratory of the Bureau of Chemistry has examined a large number of samples of American turpentine and it was found that the average rotation would be nearer 15° than 6°. Samples have been examined where the rotation was as high as 30° and it is possible to prepare fractions by distillation which would have even a higher rotation. It will thus be seen that the efficiency of the method is much reduced where such samples were used in the adulteration. A third objection is that the turpentine is not identified with certainty.

About two years ago the writer, in attempting to identify turpentine in a sample of adulterated lemon oil, had prepared the nitroso chlorides of the terpenes present with a view to obtaining other compounds with widely differing melting points. Upon examining under the microscope the crystals of the nitroso chlorides obtained it was discovered that two sets of characteristic crystals were present. Samples of the nitroso chlorides of both limonene and pinene were then prepared and a comparison with the original crystals made. The results

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[1] Semi Annual Report of Schimmel and Co., 1896.

showed that both pinene and limonene were present. Upon known samples of mixtures of lemon oil and turpentine it was found that 10 to 15 per cent. of turpentine was detectable without distillation of the sample. By distillation with the Ladenburg flask, as low as two per cent. could be detected with certainty, while with a Glinsky fractionating column of three beads, one or even one-half per cent. was detectable.

The method which has since been tried out in the laboratories of this Bureau with satisfactory results is worked as follows:[1] Fifty cc. of the samples are distilled in a Ladenburg three-bulb flask or an ordinary flask fitted with a Glinsky three-bead fractionating tube. The first 5 cc. of the distillate are mixed with an equal volume of glacial acetic acid and cooled in a freezing mixture. When cold 5 cc. of ethyl nitrite are added, the whole mixed thoroughly and while still in the freezing mixture 2 cc. of concentrated hydrochloric acid are added slowly drop by drop and the mixture allowed to remain for 15 minutes, when it is filtered on a Buchner funnel using filter paper under vacuum. The crystals are washed with ethyl alcohol, about 50 cc. (95 per cent. by volume), and the filtrate replaced in the freezing bath for fifteen or twenty minutes when a second crop of crystals will form, which may be filtered upon the first set and the whole washed thoroughly with strong ethyl alcohol.

After drying, the crystals are dissolved in the least possible amount of chloroform, and hot methyl alcohol added, until recrystallization starts, when the liquid is cooled. Finally more methyl alcohol is added and the crystals filtered off. For examination under the microscope they may be mounted in olive or some other vegetable oil. It is often found advantageous to add alcohol or acetic acid during the formation of the nitroso chloride to aid the crystallization.

The question of the natural presence of pinene in lemon oil will not be considered in this paper. The Bureau of Chemistry is now making a very thorough investigation of the question and will publish the results obtained. It is sufficient to say that wherever it has been reported, the discovery has been made only after repeated fractionation of large quantities of oil, usually ten liters or more. Such well known workers as the chemists of Schimmel and Co. have failed at times to find it after repeated attempts upon fifty liters of oil. Under the circumstances it seems impossible that pinene occurs in lemon oil in excess of minute traces never discoverable by the method here given.

Thanks are due to Mr. B. J. Howard, of the Micro-chemical laboratory of the Bureau of Chemistry, for the preparation of the micro-photographs

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[1] *Practically the method of Wallach for the preparation of the nitroso chlorides Ann. Chem.*, **253**, 251.

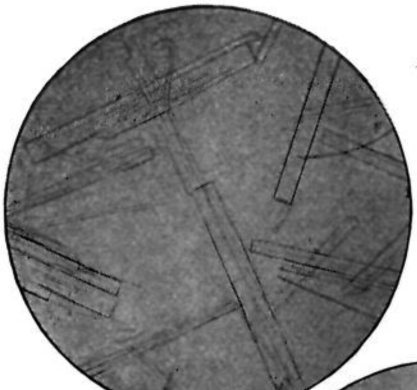

FIG. 1.

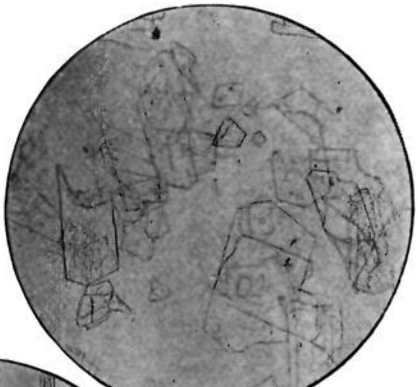

FIG. 2.

FIG. 3.

FIG. 4.

FIG. 5.

Fig. 1.—Limonene nitroso chloride crystals from lemon oil.

Fig. 2.—Pinene nitroso chloride crystals from turpentine.

Fig. 3.—Five per cent. turpentine in lemon oil, distilled in a Ladenburg flask.

Fig. 4.—Two per cent. turpentine in lemon oil, distilled with Glinsky fractionating column.

Fig. 5.—Five per cent. turpentine in limonene, distilled with a Glinsky fractionating column.

and to Mr. H. S. Bailey, of the Division of Foods, for the preparation of the crystals shown in the cuts.

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THE EFFECT OF HEAT UPON THE PHYSICAL AND CHEMICAL CONSTANTS OF COTTONSEED OIL.

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For many years, considerable reliance has been placed upon certain color reactions given by fats and oils with various reagents as a means of determining either purity or identity. Some of these tests have been exceedingly useful when applied to normal oils or fats. It has, however, been shown by many workers that the substance to which the color reaction is due is either destroyed or rendered inactive by heat. For example, Halphen's reagent fails to give a coloration with cottonseed oil which has been heated to 250–270°; and if Bechi's test be applied to an oil that has been heated to about 245°, no reduction occurs. The literature covering these points was recently summarized by one of us.

It seemed desirable to know if the application of high temperatures to cottonseed oil would produce changes in the general physical and chemical constants as well as in the color-producing capability, and therefore the work outlined below was undertaken by us. As far as we were able to ascertain there is no reference in chemical literature to this subject except the work of Tortelli and Ruggeri, which is quoted in *Bulletin No. 77 of the Bureau of Chemistry, U. S. Department of Agriculture.* Their conclusions are confirmed by our results as given below.

The following results were obtained:

	Sp. Gr. at 15.5°.		Refractive index at 25°.		Iodine value.		Saponification equivalent.		Free fatty acids calculated as oleic.	
Normal unheated oil...	0.9221		1.47509		110.1		191.8		0.06	
Temperature.	Heated 10 min.	Heated 30 min.	Heated 10 min.	Heated 30 min.	Heated 10 min.	Heated 30 min.	Heated 10 min.	Heated 30 min.	Heated 10 min.	Heated 30 min.
180°	0.9227	0.9228	1.47510	1.47510	110.0	108.1	190.9	190.8	0.053%	0.054%
220°	0.9229	0.9229	1.47518	1.47518	108.8	108.5	190.7	190.2	0.059	0.068
240°	0.9229	0.9236	1.47528	1.47548	108.4	108.5	190.4	190.6	0.130	0.260
250°	0.9236	0.9240	1.47535	1.47563	108.3	107.8	190.6	190.4	0.160	0.400
270°	0.9234	0.9242	1.47549	1.47583	106.9	106.3	190.7	190.9	0.530	0.880

The oil used by us was "winter yellow," the following constants being determined: specific gravity, refractive index, saponification equivalent, iodine value, and free fatty acids. These were determined by the usual methods, Pulfrich's refractometer being used in determining refractive index, and the Hanus method being used for iodine value. The oil was

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[1] THIS JOURNAL, 24, 1148 (1902).