Notes

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Keiichiro Hayashi and Yohei Hashimoto: Studies on the Microanalysis of Essential Oil Components. IV. The Spot Test of Essential Oil Components by Antimony Pentachloride.

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A very few work was done on the reaction between antimony trichloride and organic compounds since Kahlenberg's work[1] in which he found this color reaction with cholesterol and related compounds.

The color reaction of antimony pentachlorides was applied in the present work for the purpose of detecting essential oil components, in which dried chloroform solution of antimony trichloride (30%) or pentachloride (10%) was used and the latter was much more sensitive than the former because the latter colored even at room temperature, although heat was applied to the reactants in the case of former. Therefore, the latter should be more effective in detecting the essential oil components, such as those of nutmeg, cinnamon, fennel, xanthoxylum, and ginger.

The color reaction by both antimony pentachloride and trichloride was markedly accelerated when these were dissolved in ethylene dichloride added with 0.01% iodine than these dissolved in pure dry chloroform (cf. Table IV).

The method should be available for rapid inspection of a large number of synthetic or artificial perfumery products including bergamot, neroli, lavender, or bitter almond oil, as well as for tentative assay of natural products from which essential oil can be separated by steam distillation.

I) Essential Oil

The variation in constituents of commercial citronella oil should be due to its origin, such as Formosan, Javanese, or Ceylonese products, which was differentiated by using the color reaction difference between citronellal and geraniol. For this purpose a drop of sample is put on filter paper, followed by touching 20% sodium hydrogen sulfite solution, in order to convert citronellal to its adduct with sodium hydrogen sulfite. Then, antimony pentachloride is spotted to form the characteristic color ring which follows :

Table I. Spot Test Pattern by $SbCl_5$

Essential oil	Natural	Synthetic
Citronella	Reddish purple center, surrounded by yellowish brown color	Purple center surrounded by faint yellowish brown ring
Lavender	Reddish purple center with deep yellowish brown ring	Purple center with faintly colored ring
Bergamot	Revealed yellowish brown which gradually changes to reddish purple	Purple
Orange	Yellowish brown first, then yellowish blue and reddish purple	Reddish purple fading to grayish blue

In this way the assay of these market products was possible rapidly. The petitgrain oil (Bigarade) has shown brown to reddish purple. Its rectified terpeneless products and Paraguayan products revealed reddish brown and purple respectively, though these could be differentiated by their odor to some extent. However, the color

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1) L. Kahlenberg : J. Biol. Chem., **52**, 217(1922).

should be helpful, because it will be often difficult to distinguish the mixed product by merely testing the odor.

II) The Detection of Essential Oil Constituents in Drugs

After the steam distillation of powdered sample by the simplified apparatus demonstrated by Fig. 1, the distillate was tested by the reagent of antimony pentachloride. In the case of alcoholic extracts of vanilla or tonca beans, it is possible to treat them directly by the reagent on a filter paper.

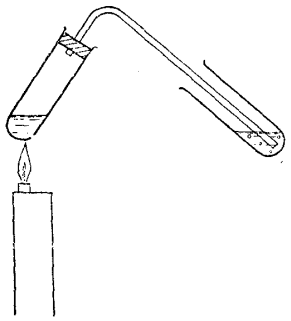

Fig. 1.

III) The Color Reaction of Essential Oil

The reaction was generally very sensitive for terpenic compounds such as citral nerol, linalool, etc., provided that 2~2.5 γ of latter two compounds be detected. In Table II, the test by antimony trichloride is also indicated in which several samples on

Table II. Color Reaction of Essential Oil Components

Essential oil	With $SbCl_5$	With $SbCl_3$
Citronella	purple, yellowish brown	reddish purple, orange yellow
Cinnamon	yellowish brown	yellow → grayish green
Star anise	brown → reddish brown	reddish purple
Xanthoxylum	yellowish brown	brown
Nutmeg	deep yellow, reddish violet	purple, orange red
Palmarosa	brown, violet	violet
Clove oil	dark violet	violet
Sandal wood	yellowish brown	reddish brown
Bay	dark violet	reddish brown
Lavender	reddish purple	yellowish brown
Bergamot	yellowish violet	yellow → violet
Geranium	yellowish brown → violet	reddish violet
Ylang ylang	dark violet	reddish brown
Fennel	yellowish brown	orange red
Benzoin	reddish brown → dark violet	violet
Vanilla beans	brown, violet	grayish green, violet

Table III. Color Reaction of Essential Oil Compound

Compound	With $SbCl_5$	With $SbCl_3$
Geraniol	yellow	orange yellow
Nerol	brown	yellowish brown
Citronellol	yellow	yellowish brown
Linalool	reddish violet	orange red
Terpineol	yellow → reddish violet	violet
Borneol	brown*	yellowish brown
Eugenol	violet	violet
Geranyl acetate	reddish brown	yellowish brown
Linalyl acetate	reddish purple	orange red
Bornyl acetate	brown	dark red
Methyl anthranilate	orange yellow	red
Anise aldehyde	yellowish brown	dark green
Citral	yellow	reddish purple
Citronellal	violet	reddish violet

* Must be heated

filter paper had to be heated in order to reveal the color. The procedure was applied also to filter paper treated by silicone resins forming remarkable color as well as in the case of usual filter paper without any preliminary treatment.

Thus, the present method was useful for the detection of major constituents, belonging to terpenoids or polyterpenoids, in essential oil.

Table IV. Identification Limit of Essential Oil Components

Solvent Component	$SbCl_5$		$SbCl_3$	
	In $CHCl_3$ (10%)	In $(CH_2Cl)_2$ with 0.01% I_2	In $CHCl_3$ (30%)	In $(CH_2Cl)_2$ with 0.01% I_2
	γ	γ	γ	γ
Geraniol	5	2	10	5
Citronellol	5	2.5	10	5
Linallol	2	1	10,[b] 5	5
Terpineol	10	5	10	10[b]
Borneol	10[a]	5	20	5
Geranyl acetate	10	5	10	10
Linalyl acetate	10	5	10	10[b]
Bornyl acetate	10	5	20	10
Methyl anthranilate	2.5	1	10	5
Anisic aldehyde	2.5	2	5	5
Citral	2.5	1	5	5
Citronellal	5	2.5	5	5
Eugenol	20	10	10	5
Nerol	2.5	1	5	2.5

a) Must be heated b) At room temperature

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Experimental

The Test of Citronella Oil with $SbCl_5$ after Treatment with $NaHSO_3$—A drop of citronella oil was put on a piece of filter paper, followed by spotting of several drops of 20% solution of $NaHSO_3$ onto the center of oil spot. By this means, terpene aldehyde (citronellal) was fixed on filter paper to form their adduct with $NaHSO_3$ while terpenes and terpene alcohols which have no carbonyl group were developed on the paper surrounding the fixed adducts in the center. The paper with sample was dried by heating at where the anhyd. $CHCl_3$ solution of $SbCl_5$ was spotted. A yellowish brown ring pattern was obtained with the center of reddish purple by which the contents of aldehyde in the essential oil could be approximately estimated. Also it was recommendable to apply the double beam self-recording densitometer which was already described in the previous paper by the present authors,[2] when more precise quantitative results will be obtained.

The Test of Crude Drugs by Steam Distillation Method—0.5 g. of finely powdered crude drugs, such as cinnamom bark, nutmeg, ginger, were placed in the bottom of test tube with 10-cc. vol., adding 5 cc. of water, and the mixture was distilled after combining glass tube and adapter indicated by Fig. 1. When the distillate amounted to 2 cc.(preferably to cut a line on the tube to facilitate the corresponding distillate measurement) by cooling the tube in water, the distillation would be completed, and the distillate was cooled by water. The whole distillate was extracted by 2 cc. of ether and the upper layer was taken out. The spot of concentrated ethereal solution on filter paper was treated with $SbCl_5$ to reveal a color.

The Test of Crude Drugs by Alcohol Extraction—Usually, benzoin, vanilla, and tonca bean are used for perfumery preparation in the state of alcoholic extract. In this respect it is useful to study the method of rapid assay of these alcoholic extracts. The extract of these drugs including star anise, fruits of *Zanthoxylum piperitum* was prepared with which $SbCl_5$ was reacted.

Summary

Amongst numerous color tests for essential oil components present, 10% chloroform or ethylene dichloride with 0.01% iodine solution of antimony pentachloride was regarded to be most excellent so far as the instantaneous spot test was concerned. The majority of compounds belonging to the category of essential oil constituents produced characteristic colors by merely touching the reagent to the sample on filter paper, without any additional treatment. (Received June 4, 1957)

2) Part III. K. Hayashi, Y. Hashimoto : This Bulletin, **5**, 76(1957).