

2. The presence of the common tissue preservatives does not interfere with the analysis of these alkaloids.

## REFERENCES.

- (1) Rising and Lynn, *Jour. A. Ph. A.*, 20 (1931), 9.
- (2) Morgulis and Levine, *Jour. of Lab. and Clin. Med.*, 5 (1920), 321.
- (3) Woodman and Tidy, "Forensic Med. and Tox." 340, 1887; and Peterson, Haines and Webster, "Legal Med. and Tox.," 545, 1923.
- (4) Ogier, Witthaus, "A Manual of Toxicology," 1911.
- (5) Witthaus, "A Manual of Toxicology," 1911.
- (6) Proelss, *Chem. Cetr.* II (1901), 1321.

## STUDIES ON THE DETERMINATION OF CAMPHOR IN CAMPHOR LINIMENT.

### III. VACUUM OVEN METHOD.\*

BY CHARLES F. POE.

#### INTRODUCTION.

In previous communications, the author with others (1, 2) has shown that the method given in the U. S. P. X for the determination of camphor in camphor liniment is not accurate. The results were found to be consistently low owing to the fact that the oil was oxidized during the heating process and consequently gained in weight. The investigation covered by this paper proposes a more accurate method for the determination of camphor in the liniment by means of the vacuum oven.

#### EXPERIMENTAL.

The materials and methods of preparation of the liniments were similar to those described in the previous papers (1, 2). The vacuum oven used was the latest type of the Freas constant-temperature vacuum oven.

A sample of camphor liniment containing 20 per cent camphor was selected for the first tests. Determinations were made using the vacuum oven and also the ordinary air oven according to the U. S. P. X method. A number of dishes made of different materials were used for the determination of the camphor and for the heating of the cottonseed oil. Table I gives the results of this series of tests.

TABLE I.—COMPARISON OF THE DETERMINATION OF CAMPHOR BY THE U. S. P. X AND VACUUM OVEN METHODS USING VARIOUS DISHES. 20 PER CENT CAMPHORATED OIL USED. 4 HOURS' HEATING.

*	Air Oven 110° C. Camphorated Oil.			Vacuum Oven 100° C. Camphorated Oil.		
	Camphor, per cent found.	Variation.	Oil alone, per cent gain.	Camphor, per cent found.	Variation.	Oil alone, per cent gain.
A	19.38	-0.62	0.95	19.74	-0.26	0.18
G	19.53	-0.47	0.82	19.89	-0.11	0.04
L	19.72	-0.28	0.50	19.92	-0.08	0.08
N	19.66	-0.34	0.56	19.81	-0.19	0.06
Pt	19.62	-0.38	0.54	19.86	-0.14	0.07
P	19.52	-0.48	0.74	19.88	-0.12	0.08

\* Presented before the Scientific Section, A. Ph. A., Philadelphia meeting, 1926, and Miami meeting, 1931.

TABLE I.—Continued.

*	Camphor, per cent found.	Air Oven 110° C.		Camphor, per cent found.	Vacuum Oven 100° C.	
		Variation.	Oil alone, per cent gain.		Variation.	Oil alone, per cent gain.
S	19.63	-0.37	0.75	19.82	-0.18	0.12
Ag	19.54	-0.46	0.62	19.85	-0.15	0.14
T	19.60	-0.40	0.66	19.92	-0.08	0.06

\* Abbreviations of kind of dish: Aluminum, A; Glass, G; Lead, L; Nickel, N; Platinum, Pt; Porcelain, P; Silica, S; Silver, Ag; Tin, T.

As may be seen from Table I, the variation from the standard for the vacuum oven method is much less than for the official method. Also the gain in weight for the oils alone was not nearly so great with the vacuum oven method. There was considerable variation for the different dishes used, especially with the official method, aluminum dishes giving the greatest error.

A number of other samples of liniment, made from different cottonseed oils, were analyzed by both methods. The results are recorded in Table II.

TABLE II.—COMPARISON OF THE U. S. P. X AND VACUUM OVEN METHODS USING DIFFERENT LENGTHS OF TIME FOR HEATING.

*	Dish Used.	Per Cent Camphor Found.					
		Air Oven 110° C.			Vacuum Oven 100° C.		
		2 hours.	4 hours.	6 hours.	2 hours.	4 hours.	6 hours.
25/6	P	24.21	24.28	24.07	24.32	24.60	24.84
..	S	24.68	24.56	24.22	24.47	24.55	24.81
..	T	24.26	24.38	24.12	24.05	24.75	24.86
..	A	24.40	24.14	23.80	24.60	24.60	24.68
10/7	P	9.66	9.60	9.60	9.46	9.88	9.95
..	S	9.76	9.84	9.64	9.14	9.88	9.89
..	T	8.76	9.60	9.68	9.34	9.79	9.88
..	A	9.46	9.26	9.28	9.37	9.41	9.80
10/8	P	8.98	9.48	9.18	9.32	9.52	9.84
..	S	9.65	9.67	9.17	9.47	9.58	9.93
..	T	9.42	9.55	9.06	9.28	9.67	9.96
..	A	9.46	9.30	8.66	9.28	9.66	9.75
10/9	P	9.46	9.48	9.36	9.10	9.62	9.86
..	S	9.64	9.68	9.25	9.24	9.70	9.81
..	T	9.20	9.25	9.20	9.27	9.67	9.88
..	A	9.35	9.21	8.89	9.50	9.52	9.80
20/13	P	19.69	19.14	19.10	19.45	19.61	19.80
...	S	19.60	19.46	19.20	19.50	19.08	19.79
...	T	19.48	19.54	19.28	19.52	19.78	19.94
...	A	19.40	19.26	19.10	19.56	19.50	19.56
20/14	P	19.58	19.60	19.36	14.92	18.46	19.80
...	S	19.52	19.66	19.42	15.96	18.90	19.83
...	T	18.92	19.48	19.18	16.35	19.49	19.85
...	A	19.34	19.70	19.00	17.82	19.72	19.82

\* First figure in this column refers to sample per cent of camphor, second number to number of oil used; the letters: P = porcelain; S = silica; T = tin; A = aluminum.

The same conclusions may be drawn from Table II as from Table I. The variation at the end of six hours for the official method was from 0.32 to 1.34 per cent, whereas that for the vacuum oven method was from 0.04 to 0.32 per cent. The use of aluminum dishes in these experiments also was found to be unsatisfactory.

A larger number of oils were next selected. These were tested for gain in weight by both methods, using tin dishes. The results which showed less gain in weight when the oils were heated in the vacuum oven are given in Table III.

TABLE III.—CHANGE IN WEIGHT WHEN COTTONSEED OILS ARE HEATED ALONE.

No. of Oil.	Air Oven 110° C.			Vacuum Oven 100° C.		
	2 hours.	4 hours.	6 hours.	2 hours.	4 hours.	6 hours.
1	+0.44 <sup>a</sup>	+0.54	+0.60	0.00	+0.06	+0.15
2	+0.63	+0.80	+1.02	-0.04	+0.04	+0.07
3	+0.31	+0.53	+0.81	-0.04	+0.05	+0.08
4	+0.32	+0.54	+0.81	0.00	0.00	+0.08
5	+0.35	+0.47	+0.64	+0.04	+0.06	+0.13
6	+0.18	+0.26	+0.28	0.00	+0.02	+0.08
7	+0.48	+0.71	+1.12	+0.04	+0.08	+0.20
8	+0.24	+0.42	+0.98	+0.08	+0.12	+0.14
9	+0.36	+0.47	+1.08	+0.08	+0.10	+0.12
10	+0.48	+0.64	+0.88	0.00	0.00	+0.06
11	+0.60	+0.78	+0.96	+0.04	+0.04	+0.10
12	+0.52	+0.68	+1.00	+0.10	+0.12	+0.18

<sup>a</sup> Results expressed in per cent.

During one set of determinations after the samples were heated for six hours in an ordinary air oven, they were placed in a desiccator. Other work prevented the weighing of these samples for several days. When the weights were taken, it was noticed that the results were abnormally low. A set of experiments was, therefore, conducted in order to determine whether the samples gain weight on standing. The results for different samples of oil are given in Table IV.

The results in Table IV indicate that samples of oil after being heated gain in weight upon standing, either in air or in a desiccator. Apparently the oxidation is

TABLE IV.—EFFECT OF EXPOSURE TO AIR OF OIL AFTER HEATING IN AIR OVEN.

Treatment of Oil.	Number of Oil Used.					
	2.	7.	8.	9.	10.	12.
Stood in air 2 hrs. (before heating)	0.00 <sup>a</sup>	0.00	0.00	0.00	0.00	0.00
Heated 2 hrs.	0.36	0.28	0.34	0.32	0.20	0.35
Stood in air 2 hrs.	0.44	0.36	0.40	0.38	0.30	0.40
Heated 2 hrs. more	0.66	0.58	0.59	0.58	0.43	0.61
Stood in air 24 hrs.	0.94	0.84	0.84	0.86	0.68	0.88
Stood in desiccator 24 hrs.	1.04	0.94	0.90	0.96	0.78	0.98
Heated 2 hrs. more	1.18	1.22	1.00	1.12	0.86	1.20
Stood in desiccator 24 hrs.	1.60	1.48	1.34	1.44	1.02	1.42
Stood in air 24 hrs.	1.78	1.64	1.44	1.62	1.18	1.61
Regular Heating.						
2 Hrs.	0.12	0.18	0.22	0.24	0.16	0.28
4 Hrs.	0.56	0.48	0.60	0.56	0.49	0.69
6 Hrs.	0.80	0.82	0.80	0.84	0.54	0.94

<sup>a</sup> Results expressed in percentage gain in weight.

hastened with the aid of heat, since the original oils showed no gain when exposed to air before heating. Similar experiments were made on samples of oil heated in the vacuum oven. The results were similar except the oxidation was not so great.

About the same results were noted when the residues from the determination of camphor were allowed to stand in air and in the desiccator.

Up to this point, it appears that six hours' heating in the vacuum oven at 100° C. is necessary to drive off all the camphor. Experiments were conducted in order to try to reduce the time required for the determination. Analyses were made on a series of samples at different temperatures. The results are recorded in Table V.

TABLE V.—EFFECT OF TEMPERATURE ON DETERMINATION OF CAMPHOR BY THE VACUUM OVEN METHOD.

Per Cent Camphor.	Number of Oil Used.	Per Cent Camphor Found.					
		Air Oven 110° C.			Vacuum Oven 100° C.		
		2 hours.	4 hours.	6 hours.	2 hours.	4 hours.	6 hours.
20	2	19.18	19.36	19.08	19.68	19.78	19.84
20	5	19.40	19.54	19.06	19.40	19.72	19.94
20	7	19.50	19.40	19.18	18.52	19.68	19.96
20	8	18.60	19.26	19.14	18.96	19.60	19.82
20	9	18.32	19.20	19.16	18.62	19.70	19.88
20	10	19.29	19.37	19.25	19.06	19.76	19.86
20	11	19.34	19.28	19.04	18.94	19.84	19.90
20	12	19.62	19.36	19.13	18.28	19.64	19.72

  

Per Cent Camphor.	Number of Oil Used.	Per Cent Camphor Found.					
		Vacuum Oven 120° C.			Vacuum Oven 140° C.		
		2 hours.	4 hours.	6 hours.	2 hours.	4 hours.	6 hours.
20	2	19.90	19.92	19.89	19.92	20.04	20.02
20	5	19.99	20.00	20.00	20.02	20.14	20.42
20	7	19.90	19.92	19.90	19.94	20.00	20.18
20	8	19.86	19.90	19.89	19.92	19.94	20.14
20	9	19.92	19.90	19.90	19.76	19.92	20.14
20	10	19.90	19.91	19.90	19.94	20.16	20.24
20	11	19.93	19.92	19.90	19.90	20.04	20.05
20	12	19.86	19.93	18.90	19.92	20.04	20.16

Apparently the oils begin to decompose about 120° C., since the results are somewhat over 20.00 per cent. To confirm this point a number of oils were heated at different temperatures in the vacuum oven. The results which are given in Table VI indicate that some slight decomposition and consequent loss in weight takes place above 120° C. in a number of the oils.

TABLE VI.—CHANGE IN WEIGHT WHEN OILS ARE HEATED IN VACUUM OVEN AT DIFFERENT TEMPERATURES.

No. of Oil.	100° C.		120° C.		140° C.	
	4 hours.	6 hours.	4 hours.	6 hours.	4 hours.	6 hours.
2	+0.08	+0.12	-0.12	-0.10	-0.20	-0.38
5	+0.12	+0.10	-0.02	+0.04	-0.23	-0.19
7	+0.06	+0.10	+0.02	+0.08	-0.08	-0.02
8	+0.12	+0.14	-0.02	+0.02	-0.10	0.00
9	+0.10	+0.12	0.00	+0.06	-0.00	-0.02
10	+0.06	+0.08	-0.10	-0.12	-0.30	-0.30
11	+0.10	+0.13	-0.03	+0.06	-0.06	+0.04
12	+0.09	+0.15	-0.05	-0.02	+0.04	-0.08

The proposed method may be summarized as follows: Place 5 cc. of camphor liniment in a tared dish, having a diameter of at least 70 mm., weigh accurately, heat at 115–120° C. for two hours in a vacuum oven, cool in a desiccator and weigh. Aluminum dishes should not be used. Also only a few minutes should elapse between the removal of the sample from the vacuum oven and final weighing.

## CONCLUSION.

A satisfactory method for the determination of camphor in camphor liniment by the use of the vacuum oven has been proposed.

## REFERENCES.

- (1) C. F. Poe, G. Lipsey and C. L. Vaughn, "Studies on the Determination of Camphor in Camphor Liniment. I. U. S. P. X Method," *JOUR. A. PH. A.*, 18 (1929), 580.
- (2) C. F. Poe and G. Lipsey, "Studies on the Determination of Camphor in Camphor Liniment. II. U. S. P. X Method for Liniments Made with Oils Other Than Cottonseed," *JOUR. A. PH. A.*, 20 (1931), 1175.

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## ALKALOIDAL REAGENTS.\* II. AROMATIC MONOHOMOCYCLIC DERIVATIVES.<sup>1</sup>

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The behavior of seventeen reagents (21, 45), has been determined with a series of the simpler benzene derivatives. Detailed precipitate and color responses are recorded in the accompanying tables. To avoid the confusion of recording the threshold dilutions which just produced color or precipitate reactions with these reagents in terms of numerical values of Molar or Millimolar concentrations, it was decided to use a code, as follows:

- a* represents a concentration of  $M/10$  or 100 Millimolar of a compound which proved to be the threshold concentration producing a reaction. The particular letter or letters designate the color of the solution or of the precipitate.
- a* represents a threshold concentration of  $M/100$  or 10 Millimolar.
- a* represents a concentration of  $M/500$  or 2 Millimolar.
- A* represents a concentration of  $M/1000$  or 1 Millimolar.
- A* represents a concentration of  $M/5000$  or 0.2 Millimolar.
- A* represents a concentration of  $M/10,000$  or 0.1 Millimolar.

In general the standard procedure previously described has been followed; however, much of this work was completed before the necessity for more accurate definition of colors was appreciated. Most of the tests gave negative results for color as well as for precipitate formation, but they were made to be certain that there would be no interference in subsequent work. Those tests which are positive, and which later prove characteristic and definite, will be repeated and color findings reported in accordance with the Mulliken nomenclature (44).

### 1. BENZENE AND HYDROCARBON DERIVATIVES.

Benzene, toluene, *m*-xylene and phenyl-benzene (diphenyl) were tested. Since none of these substances was soluble in water to the extent of 100 millimols per liter, solutions saturated at room temperature were used. All of these substances gave negative results with all of the reagents.

### 2. PHENOLIC DERIVATIVES.

Detailed results upon the compounds investigated are given in Tables I and II. Pertinent comments found in the literature follow:

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\* Alkaloidal Reagents. I, 20 (1931), 1037.

<sup>1</sup> Scientific Section, Miami meeting, 1931.