

## DIETHYLPHTHALATE II.\*

BY J. A. HANDY AND L. F. HOYT.

## I. INTRODUCTION.

During the past year we have accumulated additional data on the properties of diethylphthalate and have made a critical study of the methods for its detection, which have appeared in the literature. We are presenting the additional data thus acquired as a scientific paper entitled Diethylphthalate II.

## II. METHODS FOR THE DETECTION OF DIETHYLPHTHALATE.

Owing to the fact that many subsequent experiments have confirmed the reports made by others that the method of detection outlined in our first paper on Diethylphthalate (1) tends to give what appear to be positive tests in samples known to be free from diethylphthalate—that positive “blanks” are in other words obtained—we have made an exhaustive examination of 3 methods for the detection of diethylphthalate. These methods are:

## (A) Method of Andrew (3):\*\*

“To 10 cc. of sample in a small porcelain capsule add 5 drops of a 10% solution of NaOH; evaporate just to dryness and add 0.5 cc. of a 5% aqueous solution of resorcin, again evaporate to dryness. Add at once, without the application of external heat, 6 drops of 1.84 H<sub>2</sub>SO<sub>4</sub>, cool and dilute with 20 cc. dist. H<sub>2</sub>O made alkaline with 5 cc. of 10% NaOH.”

Andrew claims by his method to be able to secure an undeniably positive test with 0.2 milligram of diethylphthalate.

## (B) Method of Calvert (4):

“To 3 or 5 cc. of sample in a test-tube add 5 to 10 drops phenol, 10 drops of concentrated H<sub>2</sub>SO<sub>4</sub>, and heat slowly over a small flame until most of the alcohol has been driven off and the liquid assumes a red color. Cool and cautiously add 15–25 cc. distilled water when the red color will disappear and the liquid become turbid (if positive); now add an excess of sodium or potassium hydroxide. A red color denotes the presence of diethylphthalate or a phthalein in the sample. . . . The end reaction depends upon the formation of phenolphthalein by the action of hot sulphuric acid on phenol and diethylphthalate.”

“In testing a sample of alcohol or a colorless solution the test may be applied directly, but in testing whisky better results are obtained by rapid distillation and the subsequent evaporation of the distillate to a small volume on a water-bath. Good results may be obtained by shaking out with light petroleum ether a few times and then evaporating off the petroleum ether at a comparatively low temperature.”

Calvert claims that 1 cc. of a 1–1000 dilution of diethylphthalate (or 1 milligram) gives unmistakable results.

(C) Modified Mulliken Test of Handy and Hoyt. Subsequent experiments have shown that the amount of caustic used as a “fixative” can be cut down advantageously to 1 cc. of a 10% solution of NaOH. Directions are as follows:

To 5 cc. of sample in a small evaporating dish add 1 cc. of 10% NaOH solution and evaporate to dryness. Add 2 cc. of 1.84 H<sub>2</sub>SO<sub>4</sub>, heat for 1–2 min. on the steam-bath until thoroughly liquid and transfer the resulting mixture to a dry test-tube containing 0.05 Gm. resorcin. Heat for 3 minutes in an oil-bath at 160° C., shaking frequently to make sure that all of the resorcin

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is dissolved in the acid. Cool, and transfer a small portion of the contents to a large test-tube containing 50 cc. dist. H<sub>2</sub>O made alkaline with 5 cc. or more of 10% NaOH. A permanent yellowish green fluorescence shows the presence of diethylphthalate. Samples which contain any appreciable amount of saccharine matter must be extracted with petroleum ether and the test applied to this extract.

This work was undertaken, not in the spirit of justifying our original procedure, but for the purpose of bringing out to the best of our ability the advantages as well as the drawbacks of each method.

Both the Andrew method and our own are modifications of, or refinements of, the fluorescein-type test as described by Mulliken and first recommended by Lyons (2) in his article on the "Detection of Diethylphthalate in Whisky."

In the light of our subsequent experience it is evident that the cologne spirits used in the tests described in our previous paper was of a particularly high grade

TABLE I.—ALCOHOLS; COMMERCIAL, CHEMICALLY PURE, AND SPECIALLY DENATURED, COMPARATIVE BLANKS BY 3 METHODS FOR DETECTION OF DIETHYLPHTHALATE.

Alcohol used.	Handy & Hoyt method (fluorescein test; heating 3 min. at 160° C.).			Andrew method (fluorescein test; no external heat applied).		Calvert method (phenolphthalein reaction).
	Fresh.	After 48 hrs.	After 1 wk.	Fresh.	After 48 hrs.	
Cologne spirits, old sample	+, very faint	—	—	+	—	—, Colorless
Cologne spirits, stock of 2/20/23	+	—	—	Not tested (sample exhausted)		—, Colorless
Cologne spirits, stock of 4/12/23	+	—	—	+	—	—, Colorless
No. 30 denatured alcohol, new drum, recd. 3/7/23	+	—	—	+	—	—, Colorless
Merck's absolute alcohol	—	—	—	—	—	—, Colorless
Denatured Alcohols, Marked:	Fresh.	48 hrs.	1 wk.			
Denatured alcohol No. 1	+	—	—	+, Brownish green	—	—, Colorless
Denatured alcohol No. 3-A, 3/13/23	+	—	—	+, Faint	—	—, Colorless
Denatured alcohol No. 3-B	+	—	—	—, Orange-brown	—	?, Brown, turbid
Denatured alcohol No. 23-A, 5/22/22	+	—	—	—, Dark green	—	—, Colorless
Denatured alcohol No. 25, 10/5/21, Serial No. 41279	+	—	—	++, Amber	—	+, Deep pink
Denatured alcohol No. 31-A	+	—	—	—, Light amber	—	—, Colorless, turbid
Denatured alcohol No. 37, 2/21/22, Serial No. 60896	+	—	—	—, Brownish green	—	—, Pale yellow
Denatured alcohol No. 38-B, 3/6/22, Fed. Prod. Co.	+	+	—	+, Faint	—	—, Light orange
Denatured alcohol No. 39-A	+	+	—	—, Brownish green	—	?, Dark brown
Denatured alcohol No. 40	+	+	—	—, Brownish green	—	—, Colorless

since it gave truly negative blanks such as are obtained with a carefully purified and rectified absolute alcohol or other specially treated alcohols.

We wish to emphasize particularly that the tabulated results which follow, on commercial and denatured alcohols, aldehydes, ketones, and the other organic chemicals were all obtained by the same analyst. It is quite possible that other chemists employing slightly different technique and using chemicals and testing reagents from various sources might not secure exactly the same results, either as to intensity or shade obtained in the final test solutions.

II (b) Fluorescent phenomena and color reactions obtained with:

- (1) Commercial and chemically pure alcohols.
- (2) Specially denatured alcohols.

A large number of samples of commercial alcohol both cologne spirits and denatured alcohols were subjected to "blank" tests by the three methods described above, with the results as shown in the Table I. In all cases the tests were applied directly, *i. e.*, without extraction with petroleum ether, or other treatment, to a 5-cc. portion of the alcohol.

#### DISCUSSION OF RESULTS.

*Handy and Hoyt Method.*—A point of great importance is brought out by this extended series of blanks, *viz.*, that with most samples of alcohol a *temporarily* positive "blank" test is obtained by the Handy and Hoyt method when diethylphthalate is known to be absent. In the great majority of cases, however, these initially positive tests become entirely negative within 48 hours—usually in much less time—and in no case has this temporary fluorescence persisted more than 4 or 5 days. While it is true that this temporary fluorescence in blank tests when freshly made cannot be distinguished at the start from the fluorescence produced by a trace of diethylphthalate, the fluorescence obtained from diethylphthalate retains its intensity undiminished—in our own experience, exposure of such solutions to direct sunlight in unstoppered test-tubes for 2 months caused no appreciable diminution in the intensity of the fluorescence. Our results show that absolute alcohol (Merck's) gives a negative "blank" by our method. In the case of a sample of cologne spirits which gave a positive "blank" the intensity of the fluorescence was found to be directly proportional to the amount of sample used—2 cc. gave a recognizable fluorescence, while 5 or 10 cc. gave a proportionally more intense test. Some of this same alcohol was refluxed for 3 hours after the addition of 10% of its weight of solid KOH and then distilled. The distillate gave entirely negative blanks, irrespective of the amount of sample used. The addition of a small amount of commercial acetone to this purified cologne spirits caused it to give a positive blank with an intense, though temporary fluorescence.

The 3 samples each of cologne spirits and No. 30 denatured alcohol all gave positive tests, but of great variation in intensity. One of the No. 30 alcohols, a sample of poor quality from a rejected shipment, which contained acetone, gave a very intense test whereas an older sample of good quality gave only a faintly positive test. The other samples of 10 different denatured alcohols all gave initially positive blanks on 5-cc. quantities—but it is again emphasized that all of these positive tests became entirely negative on standing, mostly within 48 hours or less.

*Andrew Method.*—The results by the Andrew method are essentially parallel to those obtained by the Handy and Hoyt method. In general the intensity of the

fluorescence is less in the Andrew tests. Some of the special denatured alcohols gave negative blanks, but in other alcohols and particularly with cologne spirits and No. 30 alcohol, positive blanks with a very distinct fluorescence resulted. All of these positive blanks faded out, and somewhat more rapidly, than occurred with parallel tests by our own method.

*Calvert Method.*—With cologne spirits or denatured alcohols which do not contain interfering substances the Calvert method gives entirely negative blanks. Some of the denatured alcohols tested, especially 3-B and 39-A, contained substances which reacted with the phenol and  $H_2SO_4$  in such a way as to give dark or highly colored solutions in which it would be impossible to detect the light and fugitive pink color given in this test by small amounts of a phthalic acid derivative. Denatured alcohol formula No. 25 containing iodine gives an intense reddish violet color which might be mistaken for a positive test by the Calvert method. In general, however, this method, when applied to alcohols, may be considered to give very satisfactory negative blanks.

TABLE II.—BLANK TESTS ON ALDEHYDES AND KETONES BY 3 METHODS.

Name of aldehydes or ketones.	Handy & Hoyt method (fluorescein reaction; external heat applied).		Andrew method (fluorescein reaction; no external heat).		Calvert method (phenolphthalein test).
	Fresh.	After 4 days.	Fresh.	After 2 days.	
Aldehyde, aliphatic Formaldehyde	++	--	+, Faint dark green	--	+, Faint brownish pink
Aldehyde, aliphatic Acetaldehyde	+, Very faint	--	++, Pinkish	--	+, Distinct pink but fades very rapidly
Aldehyde, aliphatic Citral (geranial)	+	--	+	--	--, Light yellow
Aldehyde closed ring Furfuraldehyde (furfural)	++, Dark reddish brown	--	+	--	+++ Intense brownish pink, permanent
Aldehyde, aromatic Benzaldehyde	+	--	+	--	+++ Intense purplish pink, permanent
Ketone, aliphatic Acetone	+	--	++	--	--, Orange-brown
Ketone, aliphatic Musk ketone	--	--	--, Brownish green	--	--, Pale yellow
Ketone, aliphatic Methylheptenone	--	--	--, Brownish green	--	--, Pale yellow
Ketone, aromatic Acetophenone	--	--	--, Milky	--	--, Milky solution
Ketone, aromatic Camphor	+, Trace fluores.	--	--, Colorless	--	--, Colorless
Ketone, aromatic Ionone	++	--	+, Brownish green	--	--, Light orange

## II (B). (3) ALDEHYDES AND KETONES.

It was thought that impurities, particularly aldehydes and ketones, in the alcohols tested might be the cause of the temporarily positive blanks obtained

with Andrew's method and our own. Accordingly we subjected a variety of representative aldehydes and ketones, both aromatic and aliphatic, to the regular procedure of both methods as well as the Calvert method, for further comparison.

In all of these tests 1 drop, if a liquid, or 0.03 Gm. if a solid, of the aldehyde or ketone was used. The results of these "blank" tests on aldehydes and ketones, made in the absence of alcohol, are shown in Table II, on preceding page.

The tabulated results show clearly how all 5 aldehydes gave positive tests, of different degrees of intensity by all 3 methods, with the one exception of citral by the Calvert method. With our method it was the formaldehyde which gave the most intense test of the 5 aldehydes; with Andrew's method the acetaldehyde reacted most intensely and with the Calvert method closed ring furfuraldehyde and the aromatic benzaldehyde gave intense permanent tests; although the color of the final solution in these cases was a purplish red instead of a phenolphthalein pink, the test might easily be mistaken for a positive result.

All of the ketones tested gave a negative result by the Calvert test. Both acetone and ionone gave temporarily positive tests by both Andrew's method and our own, while the other four ketones gave tests negative, or practically so, by these two methods.

All of the initially positive results obtained by the Andrew method and our own became entirely negative within 48 hours. In the case of the Calvert method the positive tests with furfuraldehyde and benzaldehyde retained the peculiar purplish red color with undiminished intensity. The color so obtained is, to be sure, not the true phenolphthalein reddish pink, but might be mistaken for a positive test for a phthalein. These tests were repeated several times, always with the same results.

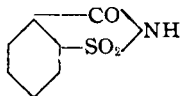
## II (B). (4) OTHER ORGANIC CHEMICALS.

### FLUORESCENT PHENOMENA AND COLOR REACTIONS RESULTING FROM CONDENSATION OF RESORCINOL AND PHENOL WITH SUBSTANCES OTHER THAN PHTHALIC ACID DERIVATIVES.

Fluorescein, the product resulting from the condensation of one phthalic acid derivative with two resorcinols, is a perfectly definite chemical compound which shows an intense, and permanent yellowish green fluorescence in alkaline solution.

Consequently when an unknown substance is condensed with resorcinol and the product dissolved in dilute alkali, a yellowish green fluorescence if obtained is normally regarded as proof of the presence of a phthalic acid derivative. It is accordingly of prime importance to know whether or not substances other than derivatives of phthalic acid will condense with resorcinol in such a way as to give a fluorescent solution which might be classed as a positive test for phthalic acid derivatives—and particularly diethylphthalate.

A recent article by Dutt (5) entitled "Dyes Derived from Saccharin. The sulphamphthaleins" called our attention to the fact that saccharin could be made to condense with a number of phenolic substances, including resorcinol, to produce compounds closely analogous to the corresponding phthalic acid—phenolic substance condensation products. Saccharin is not a derivative of phthalic acid—it is the inide of *o*-sulphobenzoic acid, thus:

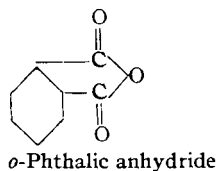
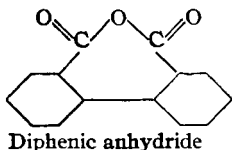


An experiment quickly showed that saccharin would condense with resorcinol when heated as in the Handy and Hoyt or Andrew diethylphthalate tests to form a product which showed a strong yellowish green fluorescence in alkaline solution. When freshly prepared such a solution would easily be mistaken for the fluorescein test made on diethylphthalate, although the saccharin-resorcinol compound (called resorcinol sulphamphthalein by Dutt) was found to gradually lose its fluorescence, so that after standing for 4-5 days such a solution is practically devoid of fluorescence, although a genuine fluorescein test as obtained on diethylphthalate will retain its fluorescence with no detectable diminution for weeks under the same conditions.

Some other chemicals including gallic, benzoic and salicylic acids were tested by heating them with resorcinol and 1.84  $H_2SO_4$  for 3 min. at  $160^\circ C$ . These compounds all gave negative tests for fluorescence. Two other more or less common compounds, succinic acid and malic acid (hydroxysuccinic acid) heated with resorcinol and  $H_2SO_4$ , resulted in condensation products which in alkaline solutions were intensely fluorescent. Succinic acid particularly gives a compound whose solution in alkali both in shade and intensity is indistinguishable *when freshly prepared* from fluorescein. Fortunately the succinic acid and malic acid fluorescent derivatives do not retain their fluorescence, their alkaline solutions like that of the corresponding saccharin compound fade out quite rapidly so that after 24-48 hours the intensity of the fluorescence is much reduced and in less than a week they have lost practically all of their fluorescence.

Lang in an article entitled "Some Interesting Reactions of Resorcinol" (7) describes the preparation of an orange-red dye, soluble in alkaline solution with a greenish fluorescence, by condensing formic acid with resorcinol in the presence of sulphuric acid. This reaction was tried out and it was found that a reaction takes place even without the application of external heat, with the evolution of considerable gas and much heat, producing a deep orange solution from which on cooling an orange-red precipitate separates out. This dye was found to exhibit a very intense yellowish green fluorescence in alkaline solution, indistinguishable when freshly prepared from that of fluorescein. This formic acid-resorcinol compound was likewise, however, found to exhibit only temporary fluorescence, the intensity being greatly diminished after standing over night, and to be practically imperceptible after standing 4-5 days.

Bischoff and Adkins (8) have recently described the preparation of still another, and entirely new, compound, very similar in its properties to fluorescein, by condensing diphenic anhydride with resorcinol. The similarity of the reaction products is to be expected on account of the close relationship of the structural formulas of diphenic anhydride and phthalic anhydride, thus:



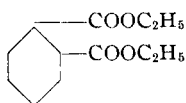
No diphenic anhydride was available for the verification of Bischoff and Adkins experiment, but an attempt was made to condense diphenyl oxide (diphenyl ether) with resorcinol, by heating at 160° C. for 3 min. with H<sub>2</sub>SO<sub>4</sub> in the usual manner. The final solution in alkali was, however, entirely devoid of fluorescence or color. It is evident that no condensation takes place with an ether and that the presence of two O-carboxylic groups or the corresponding anhydride grouping is essential for the formation of a fluorescent product comparable to fluorescein.

Comparative tests were made by heating 0.05 Gm. each of diethylphthalate, saccharin, succinic acid, malic acid, and formic acid with 0.05 Gm. resorcin and 2 cc. 1.84 H<sub>2</sub>SO<sub>4</sub> for 3 min. at 160° C. Each of the five fusions was poured into 500 cc. of water containing 25 cc. of 25% NaOH solution. The following table describes the results obtained.

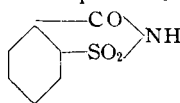
	Fresh.	After 1 week.
1. Diethylphthalate	Intense yellowish green fluorescence	Same as when fresh; undiminished intensity
2. Saccharin	Strong greenish fluorescence; solution brownish pink by transmitted light	Fluorescence entirely gone; solution brownish
3. Succinic acid	Intense yellowish green fluorescence; exactly like No. 1	Faint trace of fluorescence; solution light amber
4. Malic acid	Yellowish brown, with greenish fluorescence	Fluorescence entirely gone; solution brownish
5. Formic acid	Intense yellowish green fluorescence; exactly like No. 1	Fluorescence entirely gone; solution pale brownish yellow

Examination of the structural formulas of these first 4 compounds shows that they are substances (or derivatives of substances) which are characterized by having two COOH groups in the ortho position and that this type of compound can readily form internal anhydrides. Formic acid, the simplest of the organic acids, apparently reacts with resorcinol as though 2 molecules of it formed an anhydride.

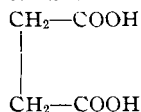
1. Diethylphthalate (deriv. of O-phthalic acid)



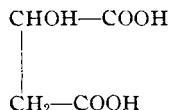
2. Saccharin (deriv. of O-sulphobenzoic acid)



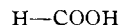
3. Succinic acid



4. Malic acid



5. Formic acid



It is possible that the solutions in alkali of the resorcinol condensation compounds of saccharin, and malic, succinic and formic acids which show this intense though temporary fluorescence could be differentiated from a solution of true fluorescein by an examination of their respective absorption spectra.

The substances saccharin, succinic acid and malic acid, which all give rise to products exhibiting a temporary fluorescence more or less resembling that of genuine fluorescein when heated with resorcinol and H<sub>2</sub>SO<sub>4</sub>, were also subjected to the Calvert test. Succinic acid and malic acid gave negative results, but as had been anticipated saccharin gave a strong reddish pink positive test. In other words saccharin will condense with phenol in the presence of H<sub>2</sub>SO<sub>4</sub> to form a

compound which is closely analogous to phenolphthalein. Dutt in his article (5) describes the condensation product of phenol and saccharin, which he calls phenol-sulphamphthalein, stating that it is pink in alkaline solution and that its sodium salt is a dark red hygroscopic solid.\* When equal quantities of diethylphthalate and saccharin were subjected to the Calvert test, final solutions of the same intensity of red or pink color were obtained which faded at the same rate. The Calvert test is fully as sensitive for saccharin, 1 mg. of which gives a strong positive test, as it is for a phthalic acid derivative and the test does not differentiate between these substances. Hence in testing an unknown by the Calvert test, if a positive result was obtained it would be necessary to prove the absence of saccharin in the portion tested in order to draw a correct conclusion as to the presence of a phthalic acid derivative. Saccharin in the form of its sodium salt, *i. e.*, soluble saccharin, is in our experience practically insoluble in petroleum ether. Hence extraction of an unknown sample with petroleum ether, which is nearly always advisable, should eliminate saccharin.

Both formic acid and diphenyl oxide when subjected to the Calvert test for diethylphthalate give an entirely negative result, a straw-colored final solution being produced. Similar negative tests were also given by gallic, benzoic and salicylic acids.

Since these three substances, saccharin, succinic acid and malic acid, might each or all be present in an alcoholic beverage (*i. e.*, a beverage not distilled) which it was desired to test for the presence of diethylphthalate, an experiment was made to determine their influence on the diethylphthalate test. A sample of sweet wine was used as the beverage.\*\*

Seven 25-cc. portions were made up as follows:

- |                                     |                                      |
|-------------------------------------|--------------------------------------|
| 1. Blank; nothing added             | 5. 25 mg. succinic acid = 0.1%       |
| 2. 25 mg. diethylphthalate = 0.1%   | 6. 25 mg. malic acid = 0.1%          |
| 3. 2.5 mg. diethylphthalate = 0.01% | 7. { 25 mg. succinic acid = 0.1% and |
| 4. 25 mg. saccharin = 0.1%          | { 2.5 mg. diethylphthalate = 0.01%   |

The seven samples were marked in code by an assistant so that the analyst might make the diethylphthalate test on the seven samples as unknowns.\*\*\*

Each sample was diluted with an equal volume of water and extracted once with 25 cc. petroleum ether. The three diethylphthalate detection tests were applied to portions of the extract of each sample. For both the Andrew and Handy-Hoyt methods 5 cc. of the petroleum ether extract (equivalent to 5 cc. of original

\* This compound is very closely related to phenolsulphonphthalein, more familiarly known as phenol red, an indicator with a  $p_H$  range of 6.8-8.4. Clark's "The Determination of Hydrogen Ions," pub. 1920, by Williams and Wilkins, states on p. 63 that phenolsulphonphthalein was first prepared by Sobon in 1898, working under Remsen. Slagle (6) describes its preparation by the fusion of the anhydride of O-sulphobenzoic acid (obtained by appropriate methods from saccharin) with phenol.

\*\* Saccharin might occur as an added sweetening agent, while succinic acid is stated to be a normal by-product of alcoholic fermentations and malic acid to occur in the free state in the juice of several fruits.

\*\*\* By placing on the tongue 3 drops of each of the original samples before extraction it was possible by the sense of taste to state with absolute conviction that No. 2 contained diethylphthalate and No. 3 saccharin. The other 5 samples could not be differentiated with any degree of certainty.



TABLE III.—DETECTION OF DIETHYLPHTHALATE IN A BEVERAGE IN PRESENCE OF POSSIBLY INTERFERING SUBSTANCES.

Calvert.	Code mark.	(a) Fresh.	Andrew. (b) After 24 hrs.	(a) Fresh.	Handy-Hoyt. (b) After 24 hrs.	Conclusion from Andrew, Handy and Hoyt tests.	Sample actually contained.
1.	Amber—negative	Brownish green; slight fluorescence	No fluorescence (—)	Distinct fluorescence	No fluorescence (—)	No diethylphthalate	Malic acid 0.1%
2.	Pink; persisted about 10 min. (+) shows presence of diethylphthalate	Intense yellow-green fluorescence	Same as (a) (+)	Intense yellow-green fluorescence	Same as (a) (+)	0.1% diethylphthalate	0.1% diethylphthalate
3.	Amber—negative	Distinct yellowish green fluorescence	No fluorescence (—)	Distinct fluorescence	No fluorescence (—)	No diethylphthalate. (By sense of taste contains saccharin)	0.1% saccharin
4.	Amber—negative	Brownish green, very slight fluorescence	No fluorescence (—)	Slight fluorescence	No fluorescence (—)	No diethylphthalate	Blank
5.	Light brown, with very fugitive pale pinkish shade; possibly (+)	Brownish green, distinct fluorescence	Same as (a) (+)	Distinct fluorescence; more intense than 1, 3, 4 and 6	Same as (a) (+)	Contains small % of diethylphthalate	0.01% diethylphthalate
6.	Amber—negative	Pale yellow, no fluorescence	No fluorescence (—)	Slight fluorescence	No fluorescence (—)	No diethylphthalate	0.1% succinic acid
7.	Light brown; no pinkish coloration observed — negative	Brownish green, strong fluorescence	Same as (a) (+)	Distinct fluorescence	Same as (a) (+)	Contains small % of diethylphthalate	0.1% succinic acid. 0.01% diethylphthalate

sample) was used; for the Calvert method the remaining 15 cc. of extract (equivalent to 15 cc. of original sample; 3 times the quantity used for either of the fluorescein reaction tests) was used. The results are shown in Table III.

When freshly prepared all the final solutions obtained by the Andrew and Handy-Hoyt tests showed varying degrees of fluorescence. Even when fresh, by both tests the No. 2 sample showed diethylphthalate by its strong and unmistakable fluorescence and the No. 5 and No. 7 samples in both cases were suspicious. After the tests had stood over night the only samples in either set which showed fluorescence were the No. 2, No. 5 and No. 7 samples. Even in the No. 5 and No. 7 test portions which contained at the most not over 0.5 mg. of diethylphthalate the fluorescence stood out clear and unmistakable and could easily be differentiated from Nos. 1, 3, 4 and 6 even when viewed from a distance.

This series of experiments, II (b) (4), has brought out the following facts:

1. A substance which shows a yellowish green fluorescence in alkaline solution is not necessarily fluorescein.

2. Saccharin (or *o*-sulphobenzoic acid or its anhydride), succinic acid, malic acid, and formic acid will condense with resorcinol to give compounds which exhibit marked, though transient, fluorescence in alkaline solution. (According to the experiments of Bischoff and Adkins, diphenic anhydride would also be included in this list of compounds.)

3. Saccharin (or *o*-sulphobenzoic acid or its anhydride) has been found to react in a manner identical with diethylphthalate in the Calvert test. Water-soluble saccharin is, however, practically insoluble in petroleum ether and hence does not interfere when testing the petroleum ether extract of a sample containing saccharin for diethylphthalate.

4. Diethylphthalate detection tests made on the petroleum ether extract of portions of a sweet wine containing, respectively, 0.1% of these substances, *i. e.*, saccharin, succinic acid and malic acid, give entirely negative results provided the final test solutions are allowed to stand over night before the interpretation of the results is made.

5. Either the Andrew or Handy and Hoyt method will differentiate correctly between a sample of sweet wine containing 0.1% succinic acid (which in our experience condenses with resorcinol to give a test solution most nearly like that of true fluorescein) and a sample containing only 0.01% diethylphthalate in addition to 0.1% succinic acid, on test portions of the samples as small as 5 cc.

*(To be concluded in next issue. Bibliography will appear at end of the article.)*

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## ADSORPTION OF IODINE FROM ORGANIC SOLVENTS BY RED PHOSPHORUS AND CHARCOAL.\*

BY NEIL E. GORDON† AND JOHN C. KRANTZ, JR.

Bancroft,<sup>1</sup> in suggesting a number of interesting research problems through the National Research Council, mentioned the work of Sistini<sup>2</sup> who had found that car-

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<sup>1</sup> Bancroft, *J. Ind. Eng. Chem.*, 13, 154, 1921.

<sup>2</sup> Sistini, *Gazz. chim. ital.*, 31, 216, 1871.