

THE DETECTION OF ROSIN IN OFFICIAL RESINS, GUM-RESINS AND BALSAMS.*

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Tests for rosin as an adulterant of official resins, gum-resins, balsams, etc., appear in nine monographs in the U. S. P. IX, *i. e.*, those of Asafœtida, Balsam Peru, Balsam Tolu, Benzoin, Guaiac, Resin of Jalap, Resin of Scammony, Oil of Cinnamon and Oil of Cade. Under Balsam of Tolu two methods are given for the detection of rosin, and under Resin of Jalap three, making thus a total of twelve instances in which rosin tests appear in Pharmacopœia IX. No tests for rosin appear in the National Formulary IV.

Of the above-mentioned tests six depend upon the reaction with copper acetate, two depend upon a modification of the well-known Liebermann-Storch reaction, one upon a color reaction with nitric acid, and one upon a similar reaction with sulphuric acid. Two depend on solubility and serve to detect the presence of other substances besides rosin and, hence, are not included in this paper. In the six instances which involve the copper acetate reaction, no two check, there being a variance either in procedure, quantity of materials used, solvents or strength of copper acetate solution. The two instances involving the modification of the Liebermann-Storch reaction are also at variance, the procedure being the same but the final color reaction in one case being red and in the other green.

The problem presenting itself, then, was a three-fold one giving rise to the following questions: "Do the tests for rosin stated in the various monographs of the U. S. P. IX give satisfactory results? Can either the copper acetate method of the Liebermann-Storch reaction be modified in such a way as to give satisfactory results as a general test applicable in all cases, or if not, can a method giving such results be found? If such a method can be found what will be its value in the detection of rosin in other than official resins, gum-resins, balsams, etc.?"

PREPARATION OF SAMPLES.

The samples listed below were prepared using 5% of rosin as an adulterant, (except in the case of No. 2, which contains 20%). This percentage was selected as a probable minimum percentage of adulteration likely to be found.

Sample 1, Guaiac with 5% rosin.	Sample 17, Powdered Guaiac with 5% rosin.
Sample 2, Guaiac with 20% rosin.	Sample 18, Powdered Resin of Jalap with 5% rosin.
Sample 3, Balsam Tolu with 5% rosin.	Sample 19, Powdered Myrrh with 5% rosin.
Sample 4, Resin of Jalap with 5% rosin.	Sample 20, Powdered Mastic with 5% rosin.
Sample 5, Balsam Peru with 5% rosin.	Sample 21, Powdered Dragon's Blood with 5% rosin.
Sample 6, Sumatra Benzoin with 5% rosin.	Sample 22, Powdered Benzoin with 5% rosin.
Sample 7, Resin of Scammony with 5% rosin.	Sample 23, Powdered Guaiac with 5% rosin.
Sample 8, Asafœtida with 5% rosin.	Sample 24, Powdered Asafœtida with 5% rosin.
Sample 9, American Styrax with 5% rosin.	Sample 25, Powdered Resin of Scammony with 5% rosin.
Sample 10, Levant Styrax with 5% rosin.	Sample 26, Powdered Jalapin with 5% rosin.
Sample 11, Venice Turpentine with 5% rosin.	Sample 27, Oil of Cinnamon with 5% rosin.
Sample 12, Copaiba with 5% rosin.	Sample 28, Oil of Cade with 5% rosin.
Sample 13, Dammar with 5% rosin.	
Sample 14, Shellac with 5% rosin.	
Sample 15, Powdered Benzoin with 5% rosin.	
Sample 16, Powdered Asafœtida with 5% rosin.	

* Scientific Section, A. Ph. A., Asheville meeting, 1923.

In Samples 1 to 14 (inclusive) attempt was made to obtain as intimate and uniform a mixture as possible. In the cases of Samples 1, 3, 4, 9, 10, 13 and 14, one part of melted rosin was mixed with nineteen parts of the melted material to be adulterated. The mixtures were well stirred for about five minutes when the heat was removed, the stirring, however, being continued until the mixtures congealed. Sample 2 was prepared in a similar manner using 20% of rosin instead of 5%. In the cases of Samples 5, 11 and 12 one part of the melted rosin was mixed with nineteen parts of the material to be adulterated, previously brought to the same temperature as the melted rosin, and the mixtures allowed to cool with constant stirring. Adulteration with rosin did not materially change the appearance of the afore-mentioned samples (1, 2, 3, 4, 5, 9, 10, 11, 12, 13 and 14) and the process of "melting in" the rosin could doubtlessly be resorted to as a means of sophistication. Samples 6, 7 and 8 require special comment.

Sample 6. One part of melted rosin was mixed with nineteen parts of melted Sumatra Benzoin and the mixture allowed to cool and congeal with constant stirring. The Benzoin did not become liquid entirely but an approximately uniform mixture was obtained. After cooling the appearance of the Benzoin was entirely changed and it is doubtful whether "melting in" could be resorted to as a process of adulteration of this drug.

Sample 7. Resin of Scammony refused to become liquid on heating, so nineteen parts of it and one part of rosin were dissolved in as small a quantity of alcohol as possible (with the aid of heat) and the mixture evaporated to dryness on a water-bath, with frequent stirring. Admixture with rosin somewhat changed the appearance of the Scammony resin. If sophistication were practiced with this drug, the rosin would doubtlessly be dissolved in the alcoholic extract of the Scammony Root before that extract is concentrated and would then subsequently be precipitated along with the Resin of Scammony when the concentrated extract was poured into water. The product thus obtained would probably bear a very close resemblance to pure Resin of Scammony.

Sample 8. Asafetida likewise does not become liquid upon heating, and heating, of course, results in the loss of volatile oil so it is questionable whether a case would occur where the rosin had been "melted in." Sample 8 was prepared by dissolving one part of rosin and nineteen parts of Asafetida in alcohol. This solution, carrying the insoluble portion of the Asafetida in suspension, was evaporated to dryness with frequent stirring. The product resulting from this process, of course did not resemble Asafœtida, and sophistication if practiced would hardly be other than mechanical.

Samples 15 to 26 (inclusive) consist of mechanical mixtures of nineteen parts of the material to be adulterated in No. 60 powder and one part of powdered (also No. 60) rosin. The samples were prepared by thorough trituration in a mortar, and repeated sifting. They doubtless represent the most common way in which adulteration is likely to occur. The admixture of 5% of powdered rosin does not alter the appearance of the powdered drugs.

Samples 27 and 28 consist of 5% solutions of rosin in the respective volatile oils.

These samples, then, offered workable material for the application of tests both on simple mechanical mixtures of the powders as well as more intimate mixtures of rosin and the pure drugs.

Where a sample number appears followed by the letter "P," it indicates that the sample used consisted of pure material from the same lot used in preparing the adulterated sample bearing the same number; *e. g.*, Sample 1-P consists of Guaiac from the same lot used in preparing Sample 1.

PRESENT PHARMACOPŒIAL METHODS.

The tests as outlined in the various monographs in the U. S. P. IX were tried with the respective samples and gave the following results. For the sake of brevity the texts of these methods are not repeated here.

TABLE I.

Copper Acetate Method.		Balsam Tolu:	
Asafœtida:		Sample 3 —	Sample 3-P —
Sample 8 +	Sample 8-P —	Liebermann-Storch modified	
Sample 16 +	Sample 16-P —	Sample 3 —	Sample 3-P —
Sample 24 +	Sample 24-P —	(purple to brown)	(purple to brown)
Benzoin:		Resin of Jalap:	
Sample 6 +	Sample 6-P —	Sample 4	Sample 4-P
Sample 15 +	Sample 15-P —	(light brown)	(light brown)
Sample 22 +	Sample 22-P —	Sample 18	Sample 18-P
Guaiac:		(light brown)	(light brown)
Sample 1 —	Sample 1-P —	Sample 26	Sample 26-P
Sample 2 —	Sample 2-P —	(light brown)	(light brown)
(very faintly green)		Nitric Acid Reaction.	
Sample 17 +	Sample 17-P —	Balsam Peru:	
Sample 23 +	Sample 23-P —	Sample 5 +	Sample 5-P —
		(green)	(yellow)
		Sulphuric Acid Reaction.	
Oil of Cinnamon:		Resin of Scammony:	
Sample 27 +	Sample 27-P —	Sample 7	Sample 7-P
Oil of Cade:		(red-brown)	(red-brown)
Sample 28 +	Sample 28-P —	Sample 25	Sample 25-P
		(red-brown)	(red-brown)

From the results in Table I it will readily be seen that the tests stated in the present monographs for Asafœtida, Benzoin, Balsam Peru, Oil of Cinnamon and Oil of Cade gave satisfactory results. The test stated in the Guaiac monograph gave satisfactory results except in the cases where the rosin was "melted in." The tests stated in the monographs for Balsam Tolu, Resin of Jalap and Resin of Scammony, however, gave unsatisfactory results. Probable explanations of some of these unsatisfactory results, and further comments on the present pharmacopœial methods will be found further in this discussion.

The second and third parts of our problem, as mentioned before, consisted of finding a suitable method applicable to all cases of adulteration with rosin of the official resins, gum-resins, balsams, etc., as well as the results that would be obtained by the use of such a method with some non-official substances. Results with non-official substances have been tabulated with the official ones in an effort to obtain brevity.

THE COPPER ACETATE METHOD.

One of the oldest and best-known methods for the detection of rosin involves the use of an aqueous solution of copper acetate. This method has been suggested by Parry¹ for use in the detection of rosin in shellac. We also find it included in six of the monographs of the U. S. P. IX, *i. e.*, those of Asafœtida, Balsam Tolu, Benzoin, Guaiac, Oil of Cinnamon and Oil of Cade, although quite an extensive variation exists throughout the six cases. The method depends upon the reaction between abietic acid anhydride, a constituent of rosin, with copper acetate, giving a copper salt of abietic acid soluble in petroleum benzin and imparting to the benzin solution an emerald-green color. The test as usually performed consists of shaking a petroleum benzin solution of the material under examination with an aqueous solution of copper acetate. The liquids are then allowed to separate, the

¹ E. J. Parry, *Chem. & Drug.*, Jan. 31, 1903.

upper or benzin layer being an emerald-green if rosin is present. Although the copper salt of abietic acid is soluble in several solvents immiscible with water, the slight solubility of several of the substances usually adulterated with rosin in petroleum benzin, and the solubility of rosin in it makes that solvent particularly adaptable to this test.

The simplest official form of the copper acetate test, excluding those listed under the volatile oils which will be considered separately at the end of this division, occurs under Guaiac. Here the crushed or powdered sample is macerated in petroleum benzin for three hours, the liquid then being filtered and shaken with an aqueous solution of copper acetate 1-1000. Referring to Table I it will be seen that the test works well enough where the sample consists of a mechanical mixture of the powders, but with samples consisting of a "melted mixture" it is quite unsatisfactory. The objectionable features of the test as given under Guaiac are: (1) the failure to give satisfactory results when rosin is "melted in," even with a mixture containing 20% rosin; (2) the length of time (three hours) necessary for the completion of the test; (3) the concentration of the copper acetate solution. In this connection it might be stated that a copper acetate solution having a concentration of 1-1000 gives a green of slight intensity while one having a 1-200 concentration (as directed under Benzoin in the U. S. P. IX) gives a very brilliant green with the same sample. It might also further be stated that even when using a concentration of 1-200 we were unable to get positive reactions with Samples 1 and 2.

The cause of the failure of the test to work on samples which have the rosin "melted in" seems to be the inability of obtaining, by mechanical means, a powder fine enough to separate particles of rosin for exposure to the solvent action of the benzin, Guaiac itself being practically insoluble in this solvent. (We were, however, as will be seen later, able to get the rosin into solution by trituration.) Parry noted the failure of the copper acetate test having a procedure somewhat similar to to the one under Guaiac, to work with samples consisting of a melted mass of shellac and rosin. He suggested¹ dissolving the entire mass first in alcohol, then adding water, thus precipitating the rosin as well as the shellac in the form of a fine powder which is filtered off, dried and macerated in petroleum benzin, the remainder of the manipulation being performed as above.

A modification of this suggestion has found its way into the present Pharmacopœia and is included in the monograph on Asafoetida. Here 25 mls of an alcoholic solution representing 5 Gm. of Asafoetida are mixed with 25 mls of petroleum benzin in a separatory funnel, 50 mls of water are added and the mixture shaken. The aqueous layer is then drawn off and the benzin layer, after being washed with water and separated, shows a green color (if rosin is present) when shaken with an aqueous solution of copper acetate 1-20. This modification of the copper acetate test gives satisfactory results, the only objection it offers being the length of time for operation which is from 20 to 30 minutes including the preparation of the alcoholic solution. Another perhaps slight objection is the concentration of the copper acetate solution, a concentration of 1-200 giving equally satisfactory results.

The copper acetate method as listed under Balsam Tolu U. S. P. IX involves maceration in carbon disulphide instead of petroleum benzin, and subsequent

¹ *Chem. & Drug.*, Jan. 31, 1903.

shaking out the filtered carbon disulphide solution with copper acetate (1-1000). One of the difficulties here is similar to that met with in Guaiac, *i. e.*, failure to work with samples containing rosin "melted in." As a melted mixture is the only kind likely to be found with this drug the objection of course is an important one. This as well as other objections to the copper acetate method as given in the Tolu monograph may be listed as follows:

- (1) Failure to give satisfactory results with samples containing rosin "melted in."
- (2) Carbon disulphide is used which occupies the lower layer making color detection difficult on account of reflection from the upper aqueous layer of copper acetate solution.
- (3) Time necessary for operation is too long.
- (4) Copper acetate solution too dilute.
- (5) Balsam Tolu contains free cinnamic and benzoic acids which are soluble in carbon disulphide. These not only interfere somewhat with the reaction between the copper acetate and the abietic acid anhydride of the rosin, but they themselves also react with the copper acetate forming cinnamates and benzoates of copper which precipitate and gradually settle into the carbon disulphide layer masking any color which might be present.

The latter objection is overcome in the case of Benzoin which also contains free cinnamic and benzoic acids. Here the Pharmacopœia directs to shake the benzoin solution obtained by maceration with the application of heat, with 10 mls of a saturated solution of NaHCO_3 . The benzoin layer is then washed with water and shaken with copper acetate solution 1-200. This method gives satisfactory results.

The problem then was to see whether the copper acetate method could be modified in such a way as to give reliable results with all samples. Several modifications of the test were attempted, such as variations in solvents, maceration and temperature. It is, however, unnecessary to repeat the results of these experiments here, save to state that the method giving the best results was as follows:

Place 1 Gm. of the sample in a small mortar. Grind or crush the sample, add 10 mls of purified petroleum benzoin and triturate well for from one to two minutes. Filter into a test-tube and add 10 mls of an aqueous solution of copper

TABLE II.

Sample 1	+	Sample 1-P	-	Sample 15	-	Sample 15-P	-
Sample 2	+	Sample 2-P	-	Sample 16	+	Sample 16-P	-
Sample 3	-	Sample 3-P	-	Sample 17	+	Sample 17-P	-
Sample 4	+	Sample 4-P	-	Sample 18	+	Sample 18-P	-
Sample 5	+	Sample 5-P	-	Sample 19	+	Sample 19-P	-
Sample 6	-	Sample 6-P	-	Sample 20	+	Sample 20-P	-
Sample 7	+	Sample 7-P	-	Sample 21	+	Sample 21-P	-
Sample 8	+	Sample 8-P	-	Sample 22	-	Sample 22-P	-
Sample 9	-	Sample 9-P	-	Sample 23	+	Sample 23-P	-
Sample 10	-	Sample 10-P	-	Sample 24	+	Sample 24-P	-
Sample 11	+	Sample 11-P	+	Sample 25	+	Sample 25-P	-
Sample 12	+	Sample 12-P	+	Sample 26	+	Sample 26-P	-
Sample 13	+	Sample 13-P	-	Sample 27	+	Sample 27-P	-
Sample 14	+	Sample 14-P	-	Sample 28	+	Sample 28-P	-

acetate (1-200) to the filtrate. Shake well and allow to separate. A green color in the benzin layer denotes the presence of rosin.

Results obtained with this method are listed in Table II.

COMMENTS ON TABLE II.

The samples containing 5% of rosin and failing to respond to the test were those of Balsam of Tolu, Benzoin, American Styrax and Levant Styrax. These samples as well as the pure samples of the same drugs all gave cloudy or flocculent precipitates with copper acetate. All of these samples contain free cinnamic or benzoic acids, or both, to which the precipitates are no doubt due, and to which the failure of the test is probably due. This suggested that possibly an insufficient amount of copper acetate was present to combine with both the abietic acid and the cinnamic and benzoic acids. The test, however, failed to give positive results when repeated with a 1-20 solution of copper acetate, in which case the concentration of copper acetate was much in excess of the quantity necessary to combine with the acids present. By repeating the method as outlined but replacing the benzin with carbon disulphide Samples 3, 6, 9, 10, 15 and 22 gave positive results in the majority of cases. As mentioned before, the objection to carbon disulphide is that its specific gravity is greater than that of water and the copper salts of cinnamic and benzoic acids formed during the test, settle into it and mask the color reaction. If the test-tubes are left standing over night or until these precipitates have settled completely, the green color is visible in the carbon disulphide layer. This necessitates quite a lapse of time and on the whole is hardly satisfactory:

The problem then was to find a solvent having a specific gravity less than one, giving the same results as carbon disulphide. Of the various solvents tried the best results were obtained with xylene which gave positive results with Samples 3, 6, 9, 10, 15 and 22 and negative results with Samples 3-P, 6-P, 9-P, 10-P, 15-P and 22-P. Precipitates are formed as before but do not interfere with the color reaction, the xylene layer assuming a green color when rosin is present. The success of the reaction seems to depend upon a greater or more rapid solubility of the rosin in xylene.

The success with xylene in the cases of samples containing free cinnamic and benzoic acids suggested it as a solvent to replace petroleum benzin in all cases. This, however, was found to be entirely unsatisfactory as the xylene dissolved many of the resins, gum-resins, etc., which interfered with the reaction when the xylene solution was shaken with copper acetate. The following rather interesting experiments show the results obtained with cinnamic and benzoic acids mixed with rosin, dissolved in xylene and in petroleum benzin when shaken with copper acetate solution 1-200. These results seem to verify the value of xylene in these particular cases, as well as prove the above negative results due to the interference of cinnamic and benzoic acids.

Sample.		Xylene.	Benzin.
Cinnamic Acid	0.100 Gm.	Green	Colorless
Rosin	0.050 Gm.	Floc. ppt.	Floc. ppt.
Benzoic Acid	0.100 Gm.	Green	Colorless
Rosin	0.050 Gm.	Slight ppt.	Slight ppt.

As petroleum benzin gives the most satisfactory results in all cases except those containing free cinnamic and benzoic acids and, as xylene serves as a suitable solvent in these cases, the method was revised to read as follows: "Place 1 Gm. of the sample in a small mortar. Grind or crush thoroughly and add 10 mils of purified petroleum benzin, except with drugs containing free cinnamic and benzoic acids, in which cases the petroleum benzin should be replaced by xylene. Triturate well from one to two minutes. Filter into a test-tube and add 10 mils of an aqueous solution of copper acetate (1-200) to the filtrate. Upon shaking well and allowing to separate, the benzin or xylene layer should not show a green color. (Rosin.)"

COMMENTS ON THE COPPER ACETATE METHOD.

The copper acetate method as finally revised gives satisfactory results and offers a simple operation in a minimum length of time, using only a 1-Gm. sample. It might well be stated at this point that the copper acetate solution should be relatively fresh and should not contain an excess of acetic acid.

It must, however, be remembered that the green color obtained with rosin is also obtainable with other substances such as Copaiba, Venice¹ Turpentine,¹ Pine Tar, etc. Generally, however, with some exceptions, resins containing oxy-acids such as abietic and oxy-copaivic give the green color. The copper acetate method, of course, is not suitable for the detection of rosin in these substances, and they, in turn if present, in substances submitted to the copper acetate test will give the characteristic green reaction. Probability of the latter, however, is perhaps slight and the method as finally revised should be of value due to its embodiment of uniformity and simplicity.

THE VOLATILE OILS.

It was not originally intended to include the volatile oils in this paper but inasmuch as rosin tests appear in the U. S. P. IX under Oil of Cinnamon and Oil of Cade, their mention here can hardly be overlooked. The copper acetate test appears in but two of the volatile oil monographs (see above). The tests as outlined in these monographs as well as the general method outlined in this paper give satisfactory results.² It is, however, hardly advisable to recommend the general method in the case of volatile oils, as these oils due to their liquid nature can readily be shaken with petroleum benzin, the solution, if the oil is miscible, or the benzin layer, if immiscible, filtered and shaken with copper acetate solution. The 1-200 concentration of copper acetate solution, however, is recommended for these tests rather than the 1-1000 as directed under Oil of Cinnamon or the 1-100 as directed under Oil of Cade.

An experience somewhat aside from this paper yet worthy of mention at this point is as follows: During our experiments we noticed that Oil of Cinnamon adulterated with rosin sometime previous and kept in a warm place did not lend itself subject to the detection of the rosin by either the copper acetate method or the Halphen color test to be mentioned later. There probably is a reaction between the abietic acid anhydride and the cinnamic aldehyde of the oil, the compound formed (which readily crystallizes out) not giving the characteristic reactions of abietic acid anhydride. It is our hope to investigate this reaction in the near future.

¹ See Table II. Samples 11-P and 12-P.

² See Table II. Samples 27 and 28, also 27-P and 28-P.

Oil of Cade also offers a rather peculiar situation which might well be mentioned at this point. Oil of Cade is more or less variable as to composition, the greater part of it usually being soluble in petroleum benzin. The filtered benzin solution, however, becomes very dark brown or often black when shaken with copper acetate solution. If after shaking with copper acetate solution, the benzin solution is diluted with an equal volume of benzin, the green color, if rosin be present, can readily be seen. If, however, the benzin solution is diluted with an equal volume of ether, the green color, if rosin be present, is brought out much more intensely. With pure Oil of Cade the color is brown. The U. S. P. IX directs ether as the diluent, and the success it offers does not warrant the inclusion of Oil of Cade under the general method.

It must, however, be remembered that Oil of Cade is more subject to adulteration with Pine Tar than with rosin.¹ Pine Tar also gives the characteristic green color with copper acetate.

There seems to be no reason for rosin tests appearing in but two of the official volatile oil monographs, as the others, under which no such tests appear, lend themselves to adulteration equally as easily as Cinnamon or Cade. Adulteration of the volatile oils with rosin, however, is perhaps very rare, rosin oil being the more frequent adulterant.

Rosin oil is usually prepared by the distillation of melted rosin. In its crude state it consists largely of hydrocarbons and some resin acids chiefly abietic. Such an oil if used as an adulterant can readily be detected by the copper acetate method. Rosin oil, however, is sometimes purified by distillation over alkali where the resin acids are removed, and such an oil consequently cannot be detected by the copper acetate method. This, of course, is an important point to be borne in mind when stating that a test is suitable for both rosin and rosin oil.

Inasmuch as rosin is probably only a rare adulterant of the volatile oils, their mention here has been brief.

THE LIEBERMANN-STORCH REACTION.

Perhaps the best-known method for the qualitative detection of rosin in admixture with other resins is the Liebermann-Storch method, sometimes also known as the Storch-Morawski method. This method consists of treating a small portion of the sample (about 0.1 Gm.) with acetic anhydride, the acetic anhydride solution being subsequently cooled and separated either with a pipette or by decantation and placed in a test-tube. Strong sulphuric acid is then allowed to flow gently down the side of the tube. At the junction of the two liquids a violet ring will immediately be formed if rosin is present; the color, however, is only transient and often disappears within thirty seconds or less, becoming a reddish brown. Perhaps a more satisfactory way of performing the test is to place the acetic anhydride solution into one of the cavities of a porcelain color-reaction plate, adding the sulphuric acid by means of a glass rod. The color changes may readily be seen against the white background and consequently be more closely observed. Although the Liebermann-Storch method is used quite extensively for the detection of rosin in shellac, etc., there has been some dissatisfaction expressed regarding its results.² These objections con-

¹ C. T. Bennet, *Phar. Jour.*, Vol. 107, p. 166.

² *Jour. Ind. Eng. Chem.*, 3, 86. *Orig. Com. 8th Int. Cong. Appl. Chem.*, XII, 106.

sist largely of its lack of sensitivity which with shellac is about 2%, the rapid disappearance of the violet color and also because cholesterol and other substances give similar color reactions to that obtained with rosin.

A modification of the Liebermann-Storch reaction has found its way into the present Pharmacopœia and may be found under Balsam Tolu and Resin of Jalap. Here, however, the acetic anhydride is replaced with glacial acetic acid and the color of the entire solution rather than of a "ring" observed. As mentioned before in this paper these pharmacopœial tests failed to give satisfactory results.

The samples mentioned before in this paper were submitted to the Liebermann-Storch reaction. Both the porcelain plate and the test-tube variation were used and the results checked against each other. The test was also repeated using glacial acetic acid as the solvent. As the results of the latter did not check in all cases with the results obtained with acetic anhydride, they have been tabulated separately. Average results of several trials are given as follows:

TABLE III.
Abbreviations.

b. brown	p. purple	v. violet
bl. black	pi. pink	tr. trace
g. green	r. red	f. faint or faintly

Where two letters appear the first should bear the suffix "ish," *i. e.*, g. b. greenish brown. A dash (-) signifies a change in color in less than 60 seconds, the colors being given in the order of their occurrence.

Sample Number.	Acetic anhydride.	Acetic acid.	Sample Number.	Acetic anhydride.	Acetic acid.
1-P	g. tr. v.	g. tr. v.	1	g.-v.-b.	g.-v.-b.
2-P	g. tr. v.	g. tr. v.	2	g.-v.-b.	g.-v.-b.
3-P	p.-b.	p.-b.	3	p.-b.	p.-b.
4-P	no color	no color	4	f. p.	no color
5-P	g.-p. b.	g. p.-p. b.	5	r. b.-g. b.	r. b.-g. b.
6-P	v.-b.	r.-b.	6	v.-b.	r.-b.
7-P	f. b.	no color	7	f. v.	no color
8-P	g.-b.	g.-b.	8	g.-r. b.	g.-b.
9-P	v.-g. b.	r.-r. b.	9	v.-r. b.	g.-b.
10-P	v.-r. b.	g. b.-b.	10	v.-r. b.	f. v.-r. b.
11-P	blue-bl.	deep v.	11	blue-bl.	blue-p.
12-P	r. p.-bl.	deep v.	12	r. v.-bl.	r. v.-b.
13-P	r.-v.	r. b.	13	v.-r.	b.
14-P	no color	very f. b.	14	f. v.-b.	no color
15-P	v.-r. b.	v.-r. b.	15	v.-b.	r. b.
16-P	f. v.-b.	b.	16	f. v.-b.	b.
17-P	f. v.-g. b.	f. v.-r. b.	17	v.-g. b.	b.-r. b.
18-P	no color	no color	18	f. pi.	no color
19-P	b.-f. p.	b.	19	r.-b.	r. b.
20-P	v.-b.	b.	20	v.-b.	b.
21-P	r.-v.	r. v.	21	r.-v.	v.
22-P	v.-b.	f. v.-f. b.	22	v.-r. b.	f. r.-r. b.
23-P	g.-b.	f. v.-g. b.	23	b.-g. b.	b.
24-P	f. g.-b.	f. g.-b.	24	f. g.-b.	b.
25-P	no color	no color	25	f. p.-f. b.	f. b.
26-P	no color	no color	26	f. p.-f. b.	no color
27-P	v.-p. bl.	b.	27	v.-bl.	f. v.-b.
28-P	v.-b. bl.	f. v.-b.	28	v.-b.	f. v.-b.

As may readily be seen from the above results, the Liebermann-Storch reaction is not at all suitable for the detection of rosin in the official resins, gum-resins and balsams. In some cases it might, however, serve to advantage as a confirmatory test. In several of the cases the color reactions of the pure drugs themselves so closely simulate that of rosin, that it is impossible, of course, to detect the presence of rosin in them. In some others where 5% rosin is present the characteristic violet color fails to appear, so taken as a whole the Liebermann-Storch test is entirely unsatisfactory for pharmaceutical work.

Another item which might be observed is the frequent variance in results obtained by the use of acetic anhydride from those obtained by the use of acetic acid. Apparently the two solvents are not interchangeable in this method, as might be supposed from the Pharmacopœia.

HALPHEN COLOR TEST.

A method rapidly gaining favor, especially in the varnish industry, consists of the use of Halphen reagent. This color reaction originally devised by Halphen for the detection of rosin oil in mineral oil, was pointed out by Foerster¹ to lend itself readily to the detection of rosin in other resins. Hicks² improved the technique of the method, and as revised by him it is quite simple of execution, gives very characteristic color changes within a few minutes and is extremely sensitive detecting the presence of 0.5% of rosin admixed with shellac, or even smaller quantities if the rosin is first separated with petroleum benzin.

The Halphen reagent consists of two solutions, *viz.*,

Solution A.

Phenol 1 part (by volume)
Carbon tetrachloride 2 parts (by volume)

Solution B.

Bromine 1 part (by volume)
Carbon tetrachloride 4 parts (by volume)

The samples mentioned before in this paper were submitted to this test, the procedure being essentially that suggested by Hicks. A small quantity of the sample (powdered) is dissolved in 1-3 mls of Solution A. This solution is then poured into one of the cavities of a porcelain color-reaction plate, until it just fills the depression, a portion of the solution soon spreading over the flat part of the plate. If some of the carbon tetrachloride is lost through evaporation, a drop or two may be added as the spreading over the flat part of the plate facilitates the observance of the color changes. Immediately a few drops of Solution B are placed in an adjacent cavity of the plate and the bromine vapors evolved allowed to impinge upon the surface of the solution in the other cavity. This may be facilitated by blowing a gentle current of air from B towards A, or the two cavities may be covered by a small bell-jar or watch glass. The color changes begin immediately with the contact of the bromine vapors and are best observed on the flat portions of the plate. The colors last long enough for satisfactory observation, the changes, however, being over within five or ten minutes.

Rosin itself gives a very intense reaction, being first green, then changing rapidly to blue and violet. The violet remains for about one or two minutes and then changes to purple, finally becoming a deep indigo or nearly black.

¹ *Ann. chim. anal.*, 14, 14.

² *Jour. Ind. Eng. Chem.*, 3, 86.

Most of the resins, gum-resins, balsams, etc., give characteristic reactions although if 5% rosin is present, as will be seen from the tabulation below, its color reactions are so intense that the color reactions of the drugs are completely masked, the characteristic rosin colors standing out very prominently, It might well also be stated that small quantities of water, alcohol or ether interfere with the sensitivity of this test. Results obtained by submitting our samples to this test are tabulated below.

TABLE IV.

Sample 1-P. First pink, then changing rapidly to red and finally becoming brown.	Sample 11. Blue, changing to violet and finally a deep purple.
Sample 1. First green, then changing rapidly to violet and then slowly to brown.	Sample 12-P. Red, rapidly changing to reddish brown and finally a deep reddish purple.
Sample 2-P. Same as Sample 1-P.	Sample 12. Red, rapidly changing to reddish brown and finally a reddish brown.
Sample 2. First green, then changing rapidly to violet, then slowly through purple and finally becoming a deep indigo.	Sample 13-P. Lilac, gradually changing to a light lilac-brown and finally a deep purple.
Sample 3-P. First pink, then rapidly violet and finally a deep purple.	Sample 13. Blue, changing rapidly to violet and finally a deep purple.
Sample 3. First blue, then a greenish blue, finally a very deep olive-green.	Sample 14-P. No color reactions..
Sample 4-P. Yellow, then gradually changing to brown.	Sample 14. Blue, changing rapidly to violet and finally to a deep purple.
Sample 4. First blue, then greenish blue, changing to violet and finally a light purple.	Sample 15-P. Pink, gradually becoming reddish brown.
Sample 5-P. First green, then an olive-green, finally becoming brown.	Sample 15. Blue, changing rapidly to violet and finally a deep purple.
Sample 5. First green, then blue, gradually changing to a blue-green and finally becoming a deep purplish black.	Sample 16-P. Slowly light blue which only becomes slightly darker on standing.
Sample 6-P. First red, then gradually changing to reddish brown and finally becoming a dark reddish brown.	Sample 16. Blue, rapidly changing to violet and finally becoming purple.
Sample 6. Blue, rapidly changing to violet and finally becoming a deep purple.	Sample 17-P. Blue-green, rapidly changing to red and finally reddish brown.
Sample 7-P. Pink, then light brown, very gradually changing to a slightly darker shade of brown.	Sample 17. Green, changing rapidly to violet and finally becoming reddish brown.
Sample 7. Blue, rapidly changing to violet and finally becoming a deep purple.	Sample 18-P. Yellow, gradually changing to brown.
Sample 8-P. Slowly light blue which only becomes slightly darker on standing.	Sample 18. First blue, then greenish blue and finally a light purple.
Sample 8. Blue, rapidly changing to violet and finally becoming purple.	Sample 19-P. Pink, gradually changing to reddish brown.
Sample 9-P. First brown, then gradually changing to green and finally becoming a deep greenish brown.	Sample 19. Blue, changing to violet, finally becoming purple.
Sample 9. First blue, then gradually becoming a darker blue and finally a deep violet.	Sample 20-P. Pink, gradually becoming reddish brown and finally dark brown.
Sample 10-P. Green, slowly changing to a deep greenish brown.	Sample 20. Blue, changing rapidly to violet and finally becoming purple.
Sample 10. Blue, rapidly changing to a darker blue and finally a deep violet.	Sample 21-P. Red, changing to reddish brown. (The solution itself is pink.)
Sample 11-P. Blue, changing to violet and finally a deep purple.	Sample 21. Blue, rapidly changing to violet and finally becoming purple.
	Sample 22-P. First red, then changing to reddish brown and finally becoming a dark reddish brown.
	Sample 22. Blue, rapidly changing to violet and finally becoming purple.

Sample 23-P. Blue-green, changing quite rapidly to violet and finally becoming reddish brown.

Sample 23. First green, then changing through violet to purple and finally becoming reddish brown.

Sample 24-P. Slowly light blue which only becomes slightly darker on standing.

Sample 24. Blue, changing rapidly to violet and finally becoming purple.

Sample 25-P. Pink, then light brown, gradually changing to a darker shade of brown.

Sample 25. Blue, then rapidly violet and finally purple.

Sample 26-P. First yellow, then gradually changing to brown.

Sample 26. First blue, then rapidly changing to bluish green and finally becoming light purple.

Sample 27-P. Yellow, gradually changing to greenish brown.

Sample 27. Blue, changing rapidly to violet and then becoming a deep purple.

Sample 28-P. Blue, changing rapidly to violet and finally becoming deep purple.

Sample 28. Same as 28-P.

It must be remembered that the intensity of the colors is somewhat dependent upon the concentration of the sample in Solution A. However, it will be observed that wherever rosin is present, except in Samples 11, 12 and 28, its color reactions render it easily detectable, especially after a little experience in the application of the test. Although the method does not give satisfactory results with Copaiba, Venice Turpentine and Oil of Cade, it nevertheless serves as a reliable reaction in the large majority of cases, and in these cases serves very satisfactorily as a general test.

CONCLUSIONS.

Methods for the detection of rosin as stated in their respective monographs in the U. S. P. IX give satisfactory results with samples of the following adulterated with 5% of rosin: Asafetida, Benzoin, Balsam of Peru, Oil of Cade and Oil of Cinnamon. Tests stated under Guaiac, Balsam of Tolu, Resin of Jalap and Resin of Scammony, however, do not give satisfactory results with corresponding samples adulterated with 5% of rosin.

The copper acetate method as revised in this paper and the Halphen color test give satisfactory results with the above-named samples (excepting Oil of Cade with the Halphen color test) and serve very well as general tests for the detection of rosin in these drugs.

Both methods also give satisfactory results in the detection of rosin in the following materials some of which are official: American Styrax, Levant Styrax, Dammar, Shellac, Myrrh, Mastic, Dragon's Blood and Jalapin. They do not, however, give satisfactory results with Balsam of Copaiba and Venice Turpentine, the presence of resin acids, similar to abietic acid, in these particular drugs, probably being the cause of the failure.

There is a question as to which of the two methods, the copper acetate method or the Halphen color test, is to be preferred. For general pharmaceutical testing, however, the writer recommends the former, due to its simplicity, the fact that only one reagent is necessary, and also that previous experience is hardly necessary to detect the color change. In the case of Oil of Cade, however, the modification of the copper acetate method as it exists in the present Oil of Cade monograph is recommended on account of the peculiar nature of Oil of Cade; this being the only exception to the rule.

In conclusion, the writer takes this opportunity to thank Professor E. N. Gathercoal for his valuable suggestions offered during the progress of this work.