to note that at the end of 24 hours' dialysis there was a precipitate in the solution remaining in the dialysis bag in the case of neoarsphenamine, but none in the case of sulpharsphenamine. This precipitate was flocculent in character and was readily soluble in sodium hydroxide.

TABLE I.

Compound.	Total Arsenic Present—Mg. before Dialysis.	Total Sulphur Present—Mg. before Dialysis.	Undialyzed Material. Arsenic. Mg.	Arsenic. %	Sulphur. Mg.	Sulphur. %
Neoarsphenamine	178.2	56.4	111.0	66.3	10.4	18.5
Sulpharsphenamine	197.5	95.4	72.4	38.4	29.7	31.1

CONCLUSIONS.

1. These results show that neoarsphenamine has a larger undialyzable arsenic content than sulpharsphenamine.

2. It is also shown that the sulphur content of sulpharsphenamine is less readily removed by dialysis than that of neoarsphenamine.

3. In the course of the dialysis of neoarsphenamine a portion of the material remaining undialyzed precipitates in the dialysis bag. This is not true in the case of sulpharsphenamine.

4. The previous conclusion of a fundamental structural difference between neoarsphenamine and sulpharsphenamine is confirmed.

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THE POTASSIUM MERCURIC IODIDE REAGENTS FOR ALKALOIDS.

BY JANET TRAVELL, M.D.

A number of potassium mercuric iodide solutions have been recommended as precipitating reagents for alkaloids. Of these, Mayer's reagent is the most widely used and is regarded as an exceedingly sensitive qualitative solution for alkaloids in general. It was found, however, that this reagent would not detect codeine unless present in a concentration of at least 1 in 5000 parts, but that modification of the reagent rendered the reaction with codeine and other alkaloids much more delicate. These experiments show that Mayer's reagent, which is advocated as a qualitative test solution by the United States Pharmacopœia X and by textbooks generally, is probably the least sensitive of the potassium mercuric iodide reagents which have been described. It seemed worth while, therefore,

to review the literature in some detail, which I have found rather inaccessible, and to call attention to certain practical points concerning the use of these reagents, which may not be familiar to those not working constantly with them, or to whom the early literature is not available.

It is conceded that Winckler, court pharmacist at Zwingenberg (1), in 1830 prepared the first iodomercurate of an alkaloid (2). The introduction of the potassium mercuric iodide solutions as general qualitative reagents for the alkaloids is attributed to A. von Planta Reichenau (3), who in 1846 in a dissertation at Heidelberg gave them a prominent place among the alkaloidal reagents (4). After a lapse of several years, interest in this type of alkaloidal reagent reappeared in several parts of the world. Delfs (5) in 1854 observed that twelve non-volatile alkaloids were precipitated by his potassium iodomercurate solution, some even in high dilution, but he did not state the strength of his reagent. Nessler (6) in Germany in 1856 adapted the potassium mercuric iodide reagent as a qualitative test for ammonia in strongly alkaline solution, incidentally calling attention to its property of precipitating certain alkaloids in acid or slightly alkaline solution. de Vrij (7) in Holland in 1857 stated that 1/50,000 grain of strychnine could be detected if a drop of liquid were suspended in a capillary tube and a solution of the iodide of mercury and potassium added. Groves (8) in England in 1858 described the properties of a class of compounds, the bromo- and iodomercurates of the alkaloids, which he believed had escaped general attention. He did not directly describe the reagent which he used, but studied the properties and composition of the crystalline precipitates obtained with nine alkaloids.

Finally, in 1862 Valser (9) in Paris and Mayer (3) in New York published reports almost simultaneously on the use of potassium mercuric iodide solutions as general alkaloidal reagents. Valser alluded to de Vrij as the originator of the test, Mayer, to Groves. Valser's thesis, dated July 22nd, was the prize essay of the Société de Pharmacie (not a student dissertation) for the year 1862 (10). He advocated the use of a reagent which he prepared by saturating a 10 per cent (10:100) solution of potassium iodide with mercuric iodide to detect the presence of an alkaloid in an extract obtained by the method of Stas. He analyzed some of the alkaloidal precipitates and arrived at practically the same general formula for them as had Groves. He also used his reagent quantitatively to determine the molecular equivalents of certain alkaloids, and concluded that quinidine was an isomer and not a polymer of quinine. He noted that the presence of albumins and extracted principles might interfere with the results when the reagent was employed for the quantitative titration of alkaloids. Abstracts (11, 12, 13) of Valser's thesis promptly appeared in several journals in different countries, and it is difficult to understand why the Valser reagent received so little recognition except that none of these abstracts contained the exact formula for his reagent, and so far as I have been able to learn, his original paper was not printed in one of the scientific journals, nor did any further papers by Valser follow.

Mayer's (3) original paper on this subject was read at the annual meeting of the AMERICAN PHARMACEUTICAL ASSOCIATION in August 1862, and the next year an abstract (14) was published in the same number of the PROCEEDINGS as was a brief abstract (11) of Valser's thesis. Mayer claimed to have developed a new method for the volumetric estimation of alkaloids by means of titration with his potas-

sium mercuric iodide solution. Mayer's reagent is essentially a standard solution of potassium mercuric iodide in an excess of potassium iodide for quantitative use, which Mayer described as a tenth-normal solution of the iodohydrargyrate of potassium prepared by dissolving 13.55 Gm. of corrosive sublimate and 49.8 Gm. of potassium iodide in one liter of water. This was based on the equation (4):

$$HgCl + 3KI = KI.HgI + KI + KCl \ (Hg = 100).$$

The Pharmacopœia of the United States (15) directs essentially the same formula for the preparation of Mayer's reagent at the present time. Mayer unquestionably popularized the use of the potassium mercuric iodide solution for the quantitative determination of alkaloids, as his first article was followed almost at once by others (16, 17, 18) dealing with the details of the method, the determination of the alkaloidal molecular equivalents, the limits of sensitivity of the test, and the alkaloidal content of pharmaceutical preparations and vegetable extracts such as opium. Although the correctness of certain of the molecular equivalents obtained by Mayer has been confirmed by others (4), Mayer's method for the quantitative estimation of alkaloids had eventually to be abandoned because of the difficulty in fixing the end-point of the reaction. Nevertheless, the general use of Mayer's reagent for qualitative work has persisted up to the present time in spite of the availability of more sensitive types of potassium mercuric iodide reagents.

Regarding its usefulness for qualitative purposes, Mayer (16) found that distinct reactions were obtained with his reagent in solutions containing the following concentrations of various alkaloids (to quote from his paper): "atropia 1:7000, conia 1:8000, morphia 1:2500, narcotina 1:60,000, strychnia 1:150,000, brucia 1:50,000, nicotia 1:25,000, quinia 1:125,000, quinidia 1:50,000 and cinchonia 1:75,000." He stated that precipitates occurred in acid, neutral or slightly alkaline solution, apparently with equal sensitiveness. He reiterated that the presence of albumin did not interfere with the test: "Iodohydrargyrate of potassium, or a solution of corrosive sublimate in iodide of potassium, is not affected by tannin, albumen, . . . etc." (3), and "Iodohydrargyrates . . . differ from all other precipitants of the alkaloids, which as a rule do not allow the presence of starch, gum, albumen or tannic acids" (16). Mayer's observations were at fault in that he did not note that the reaction with some alkaloids, such as nicotine, is much less sensitive in slightly alkaline than in acid solution; he was not aware that albumin and other proteins yield precipitates with his reagent even in fairly low concentration; and he did not recognize that his reagent contained an excess of potassium iodide which rendered the alkaloidal precipitates soluble in an excess of the reagent.

In fact, a decade later, Tanret (19) utilized the precipitation of albumins by a potassium mercuric iodide solution for the quantitative estimation of albumin in urine. His reagent is still in vogue as a very delicate qualitative test for this class of compounds (20). Tanret was particular to note that although Valser had observed the precipitation of albumin by potassium mercuric iodide, he had not referred to the study of albumin in urine or elsewhere by means of his reagent (21).

Tanret, who must have had access to Valser's original article, also reinvestigated the subject of the qualitative use of potassium mercuric iodide reagents for

alkaloids (21). He noted that Mayer's solution contained an excess of potassium iodide, while in the reagents described by other authors there was a slight excess of mercuric iodide. He pointed out that the concentration of the potassium iodide solution from which the reagent was prepared affected the composition of the reagent. Thus in a solution saturated with potassium iodide, the double iodides which he depicted as $(HgI)_2KI$ and HgI.KI were formed, for under these conditions 3 mols of mercuric iodide required 2 mols of potassium iodide for solution; but owing to secondary decomposition of the salt $(HgI)_2KI$ a dilute solution ultimately contained only the iodide HgI.KI. He found that 10 Gm. potassium iodide in 10 per cent solution dissolved 14.73 Gm. mercuric iodide at 20° C., instead of the theoretical 13.68 Gm. required for the formation of the iodide HgI.KI, or the 21.44 Gm. of the iodide $(HgI)_2KI$ alone. He concluded, therefore, that the solution of potassium iodide directed in the preparation of Valser's reagent was sufficiently concentrated to retain in solution a certain amount of the compound $(HgI)_2KI$.

Tanret (21) compared the sensitiveness for various alkaloids of Mayer's and of Valser's reagents. His purpose in making this comparison is implied in his statement: "I observed that the iodohydrargyrates of the alkaloids are all more or less soluble in iodide of potassium, from which it must be concluded that the Mayer's solution which contains an excess of this latter salt is inferior to that of Valser." Alkaloids were tested both as the free base and as the salt, and the results obtained with both reagents were contrasted in a table which I have reproduced in part (Table I).

TABLE I.—RESULTS OF TANRET'S TESTS WITH MAYER'S AND VALSER'S REAGENTS.*

	Mayer's Solution.	Valser's Solution.
Atropine, base or salt	7,000	40,000
Cocaine, base or salt	60,000	240,000
Codeine, base	3,000	40,000
salt	8,000	40,000
Morphine, salt	2,000	10,000
Nicotine, base	1,200	160,000
salt	17,000	600,000
Pilocarpine, salt	9,400	60,000
Quinine, base	150	360,000
salt	180,000	480,000
Strychnine,[1] salt?	50,000	150,000

* The table indicated the number of parts of water in which the alkaloid might be dissolved and yet yield a distinct precipitate with the reagents.

[1] Added from the text of the article.

Tanret (21) also studied some of the properties of the alkaloidal precipitates, and mentioned several substances which might interfere with the reaction. He recommended that tests with Valser's reagent be carried out in neutral solution, and suggested that an alkaloid might be detected in the presence of albumin in acid solution by heating to boiling, filtering while hot and observing the reappearance of the alkaloidal precipitate in the cold.

Quite recently attention has been redirected by Munch, Crossley and Hartung (22) to the fact that Mayer's reagent is not the most delicate possible potassium

mercuric iodide reagent, that the sensitivity of successive lots may vary, and therefore they have suggested some modifications in its method of preparation to render it more sensitive. Fulton (23) in a classification of the reactions of 91 precipitating agents with alkaloids mentions four types of potassium mercuric iodide solutions which he terms "Mayer's reagent, concentrated Mayer's reagent, acid Mayer's reagent, and Mayer's and KI." All these reagents are prepared from mercuric iodide rather than from mercuric chloride which Mayer used, and the second one, prepared from 10 Gm. KI in 100 cc. water saturated with HgI_2 (about 15 Gm. required), very closely resembles Valser's reagent.

In spite of the marked superiority of Valser's over Mayer's reagent, which Tanret demonstrated so strikingly, none of the European Pharmacopœias, not even the French, recommend the use of Valser's reagent, and several of them (24) describe what is essentially Mayer's reagent as a qualitative test solution for alkaloids.

EXPERIMENTAL.

Reagents.—I. Mayer's reagent was prepared according to the directions in the United States Pharmacopœia X: mercuric chloride 1.358 Gm., potassium iodide 5.0 Gm., distilled water to make 100 cc., amounts nearly identical with those in Mayer's original formula.

II. Following a search of the literature with reference to the potassium mercuric iodide reagents, the general description of Valser's reagent was found (21). A reagent was then prepared by adding slowly from a burette a 10 per cent solution (W/V) of potassium iodide to a known weight of red mercuric iodide until the latter just dissolved. Under these conditions it was found that at 20° C., 10 Gm. of potassium iodide (U. S. P.) would dissolve almost exactly 14 Gm. of mercuric iodide (U. S. P.). This differs slightly from the figure, 14.73 Gm., obtained by Tanret; but 10 Gm. of the former salt would not accomplish the solution of 14.73 Gm. of the latter even when allowed to remain in contact with it for 24 hours, and after standing in contact with this excess of mercuric iodide, the solution contained free iodine. It is not clear from the references available by what method Valser's reagent was prepared. In any case, the reagent prepared by the method of titration, by which the complete solution of the mercuric iodide is just effected by the potassium iodide solution, and which proved to be in general the more delicate, will be referred to throughout this paper as the Valser reagent.

The Valser reagent is a clear, bright yellowish green, heavy liquid with a specific gravity of 1.1811 at 25° C. When cooled to a temperature of 4° C., red mercuric iodide does not separate out, nor is there any change in the appearance of the solution. The reagent does not contain free iodine, nor does any develop on standing. On diluting the reagent several times with distilled water, red mercuric iodide precipitates. No precipitate occurs when Mayer's reagent is similarly diluted. The Valser reagent does not decompose nor deteriorate with reference to its alkaloidal sensitivity when kept on a shelf in the light (not in direct sunlight) for at least three months, and probably longer.

A study was made of the relative sensitiveness of Mayer's and Valser's reagents for some of the commoner alkaloids in pure solution. Because of the marked solubility of the precipitates in an excess of Mayer's reagent, and in order to avoid undue dilution of the alkaloid, the conditions were arbitrarily fixed so that for each test 0.5 cc. of the reagent was added to 5 cc. of the alkaloidal solution. Tests were usually performed both in neutral and in acid solution; for the latter, dilutions of the alkaloid were made with tenth-normal sulphuric acid. It was noted that whereas the relatively concentrated solutions of the alkaloids yielded a definite precipitate with the reagents, in the more dilute solutions only a characteristic bluish fluorescence appeared, similar to that shown by pure solutions of quinine and quinidine. Slight degrees of fluorescence could be seen only when the test-tube was held against a background in a suitable light, and not by artificial light. Disappearance of fluorescence, rather than the absence of a precipitate, was considered as marking the limit of sensitivity. Because of the slowness with which fluorescence may develop when the alkaloid is present in low concentration, observations were made for about ten minutes.

The results of the comparison between the two reagents are shown in Table II. It was found that in the case of each of the nine alkaloids examined, Valser's reagent permits the detection of the alkaloid in much lower concentration than does Mayer's reagent. The relative sensitive-

TABLE II.—LIMITS OF SENSITIVITY OF MAYER'S AND VALSER'S REAGENTS.*

Alkaloid.	Lowest Concentration of the Alkaloid Which Can Be Detected by		Relative Sensitiveness of Valser's / Mayer's.
	Mayer's Reagent. One Part in	Valser's Reagent. One Part in	
Atropine sulphate	6,000	43,000	7.2
Cocaine hydrochloride	125,000	600,000	4.8
Codeine phosphate	5,500	43,000	7.8
Morphine sulphate	1,300	7,000	5.4
Nicotine	15,000	225,000	15.0
Pilocarpine hydrochloride	16,000	80,000	5.0
Quinidine sulphate	300,000	1,500,000	5.0
Quinine sulphate	300,000	1,500,000	5.0
Strychnine sulphate	100,000	500,000	5.0

* 5 cc. of the alkaloidal solution acidulated with sulphuric acid and 0.5 cc. of the reagent were used for each test, except in the case of pilocarpine and atropine which were tested in neutral solution.

ness of the former to the latter ranged from about 5 to nearly 8 times, with the exception of nicotine for which Valser's was approximately 15 times as sensitive as Mayer's reagent.

III. In order to test the effect of dilution of the reagent upon alkaloidal sensitivity, a third reagent, which we shall call the dilute Valser reagent, was prepared by the same method as employed for the Valser reagent, but using a one per cent solution of potassium iodide for titration of the mercuric iodide instead of a 10 per cent solution (W/V). Under these conditions, 10 Gm. of potassium iodide (U. S. P.) dissolves only 11.8 Gm. of mercuric iodide (U. S. P.) instead of 14.0 Gm. The dilute Valser reagent does not contain free iodine. On dilution with distilled water, mercuric iodide does not separate out.

A comparison was made of the sensitiveness for alkaloids of the dilute Valser reagent with that of the undiluted. It was found the ratio of sensitivity of one reagent to the other was not constant for the group of alkaloids named in Table II; thus the alkaloidal sensitivity of Valser's reagent ranged from 1.5 times that of the dilute reagent for quinidine to 6.5 times, for nicotine. The dilute reagent was in all instances more sensitive for these alkaloids than was Mayer's reagent.

Alkaloidal Iodomercurates.—The precipitates formed by Mayer's and Valser's reagent with the alkaloids listed in Table II are readily soluble in 10 per cent potassium iodide solution (W/V), dilute ethyl alcohol and tenth-normal sodium hydroxide. A concentration of alcohol as low as one or two per cent may diminish the sensitivity of the test. The precipitates are moderately or readily soluble in concentrated acetic and hydrochloric acids, but much less so in these acids when dilute. In dilute sulphuric acid the precipitates appear to be not at all soluble, except those of pilocarpine, which is quite soluble in this acid when as dilute as tenth normal, and of atropine, which is moderately soluble. The behavior of pilocarpine is peculiar among the alkaloids tested in that its iodomercurate is exceedingly soluble in dilute acetic, hydrochloric and sulphuric acids. All the precipitates of this group of alkaloids disappear on heating to boiling or in some instances at a temperature considerably lower than the boiling point.

Tanret noted that Mayer's and Valser's reagents yielded precipitates in much lower concentrations of certain of the alkaloidal salts than of the corresponding free bases. This observation was confirmed to some exent by the author, but the differences were not so striking as those obtained by Tanret. It was found that when nicotine base was dissolved in distilled water, the limit of sensitivity for Mayer's reagent was about 1:1300 and for Valser's reagent, 1:25,000; whereas in a solution of nicotine sulphate, prepared on the basis of the formula $C_{10}H_{14}N_2.H_2SO_4$, the limits were 1:3000 and 1:100,000, respectively. Solutions of quinine and strychnine bases, however, gave precipitates with both Mayer's and Valser's reagents in only slightly higher con-

centrations than did similar solutions of their salts. The lower sensitivity of the reagents with nicotine base, as compared with the salt, is probably due to the alkalinity of the solution.

Proteins.—The behavior of several proteins, namely, egg albumin, serum albumin, hemoglobin and gelatin, was studied with the various potassium mercuric iodide reagents described: Mayer's, Valser's and the dilute Valser's, the last two of which contain little or no excess of potassium iodide. In addition, tests were made with a reagent similar to Mayer's but containing a smaller excess of potassium iodide, prepared according to the formula: mercuric chloride 1.358 Gm., potassium iodide 3.422 Gm., distilled water to make 100 cc.

Colloidal solutions of the several proteins were prepared in distilled water. Precipitation in neutral solution did not occur with any of the potassium mercuric iodide reagents; precipitates appeared only in acidulated solution (sulphuric acid). In the case of each of the proteins, the limit of sensitivity was the same for all four reagents. The highest dilution of egg albumin which gave a positive result was approximately 1:70,000, of serum albumin, 1:15,000, of hemoglobin, 1:40,000 and of gelatin, 1:400,000.

The protein iodomercurates are difficultly, if at all, soluble in 10 per cent potassium iodide solution, or in ethyl alcohol, and they are intensified on heating, facts which serve to differentiate them sharply from the alkaloidal precipitates. The protein precipitates, like those of the alkaloids, dissolve readily on alkalinization with sodium hydroxide.

Tanret made the difference in the effect of heat on the alkaloidal and protein precipitates the basis of a method (described above) for the detection of an alkaloid in the presence of albumin. Although this method serves for alkaloids in moderately dilute solutions, it was found that the process of filtration necessary to remove the albuminoid precipitate markedly reduces the sensitiveness of the test for the alkaloid, probably owing to adsorption.

DISCUSSION.

There is a lack of agreement regarding the composition of aqueous solutions of potassium mercuric iodide. Briefly, it appears that a number of complex iodides may be formed upon the addition of a solution of potassium iodide to mercuric iodide or chloride. Five complex salts in all have been reported (25). On the basis of results obtained by a number of investigators, Dawson (26) concluded that when employing dilute solutions of potassium iodide in the preparation of these reagents, the tetraiodide, $2KI.HgI_2$, is the chief complex salt present, and that as the concentration of potassium iodide is raised and the relative proportion of mercuric iodide in the solution increases, this complex iodide is gradually transformed into one containing a relatively larger amount of mercuric iodide, either $3KI.2HgI_2$, or $KI.HgI_2$ together with equimolar quantities of $2KI.HgI_2$, probably the former. Exception to these conclusions has been taken by Dunningham (27) who calculated that in a 3-component system $KI–HgI_2–H_2O$ at 20° to 30° C., potassium mercuric triiodide, $KHgI_3$, and its hydrate, $KHgI_3.H_2O$, were the only complex iodides formed. Both potassium mercuric triiodide and tetraiodide have been prepared and their properties studied; the former is decomposed by water with precipitation of red mercuric iodide, while the latter is relatively stable (25). On treating mercuric chloride with potassium iodide as in Mayer's reagent, a complex iodide is first formed from which mercuric iodide rapidly separates owing to a secondary reaction with the mercuric chloride (28). The general conclusion is that aqueous solutions of mercuric iodide in potassium iodide contain the complexes $2KI.HgI_2$ and $3KI.2HgI_2$, and that under certain conditions, when using saturated or very concentrated solutions, potassium mercuric triiodide, $KI.HgI_2$, may also be formed.

Two factors in the main seem to influence the sensitivity of the potassium mercuric iodide reagents for alkaloids: the presence of an excess of potassium iodide

in which the precipitates are soluble, the nature of the complex iodide, which is determined by the relative amounts and concentration of the reacting salts, and probably by the temperature and a variety of other conditions which have not been adequately determined. The fact that on diluting the Valser reagent mercuric iodide precipitates out, whereas on dilution of the relatively dilute Valser reagent (Reagent III) no such precipitate is obtained, suggests the presence in the former of the triiodide, $KI.HgI_2$, and in the latter, of only the more stable tetraiodide, $2KI.HgI_2$. That the difference in sensitivity of the undiluted and dilute Valser reagents does not vary uniformly for the alkaloids tested, suggests further that these two complex salts behave differently toward these alkaloids, yielding alkaloidal iodomercurates with different solubilities.

Chemical analyses of the alkaloidal iodomercurates are comparatively rare. François and Blanc (29) prepared crystalline iodomercurates of eleven alkaloids. The majority of these contained one molecule of mercuric iodide in combination with one molecule of the iodohydrate of the alkaloid (HgI_2.Alkaloid.HI or 2HI), but three other types were described.

Certain differences obtain for the absolute limits of sensitivity of Mayer's and Valser's reagents for alkaloids as determined by Mayer, Tanret and myself. This is not surprising since it is certain that in 1863 Mayer was working with impure preparations of some of the alkaloids; Tanret likewise probably did not have specimens identical with those available at the present time. Furthermore, slight differences in the preparation of the reagents, especially in the relative amounts of potassium iodide and mercuric iodide, or chloride, cause considerable variation in sensitiveness. When using Mayer's reagent, the relative amounts of the alkaloidal solution and the reagent may also influence the results. The degree of acidity of the solutions constitutes another factor. In the present investigation, disappearance of fluorescence rather than absence of a precipitate was used as an end-point in determining the limits of sensitivity, whereas Tanret refers to a "distinct precipitate," a fact which would serve to explain possibly the higher limits of sensitivity obtained by the author with Valser's reagent, but not the lower limits for morphine and nicotine. Tanret, nevertheless, found that for the salts of seven alkaloids excluding nicotine, Valser's reagent was on the average 4.5 times as sensitive as Mayer's reagent, while the author determined the average ratio for the same alkaloids with the addition of quinidine to be 5.6 times.

The Valser reagent may prove useful for the quantitative estimation of small quantities of an alkaloid not in perfectly pure solution. It may also be possible to determine with relative ease any appreciable decomposition occurring in stock solutions of the alkaloids during a period of time. Thus, a solution of codeine sulphate did not alter in its behavior toward the reagent during a period of two months; a solution of morphine sulphate, on the contrary, became markedly more sensitive on standing. This would seem to indicate the decomposition or oxidation of the morphine into a compound or compounds detectable in higher dilution by the potassium mercuric iodide reagents than morphine itself.

For qualitative use the Valser reagent is to be preferred to Mayer's reagent, for the former yields a positive test in much lower concentrations of the alkaloids than does the latter, and possesses the added advantage that at the same time it is no more sensitive than is Mayer's reagent for certain protein impurities. Testing

with both these reagents provides an additional means of distinguishing between the iodomercurates of proteins and those of the alkaloids.

SUMMARY AND CONCLUSIONS.

1. A potassium mercuric iodide reagent, which closely resembles a reagent described by Valser, the exact formula for which was not available, was prepared by slowly adding a 10 per cent (W/V) solution of potassium iodide to red mercuric iodide until the mercuric iodide was just completely dissolved. Under these conditions, 10 Gm. of potassium iodide made up to 100 cc. in distilled water dissolves approximately 14.0 Gm. of mercuric iodide at 20° C.

2. The Valser reagent is much superior to the widely used Mayer's reagent as a qualitative test solution for alkaloids. For the nine alkaloids tested in pure solution, the former reagent was found to be from 4.8 to 15.0 times as sensitive as the latter.

3. The alkaloids investigated yielded a positive test with the Valser reagent in concentrations which ranged from approximately 1:7000 for morphine sulphate to 1:1,500,000 for the sulphates of quinine and quinidine.

4. Each of several proteins, which in low concentrations also form precipitates in the potassium mercuric iodide solutions, possesses virtually the same limit of sensitivity with all these reagents prepared regardless of their concentration or the presence of an excess of potassium iodide. Thus Valser's reagent was not more sensitive than Mayer's reagent for any of the proteins tested.

5. Attention is directed to the variability in the individual behavior of the alkaloids with solutions of potassium mercuric iodide. For example, the exceptional solubility of the iodomercurate of pilocarpine in dilute sulphuric acid (tenth normal) is pointed out, whereas the solubility of the iodomercurate of nicotine diminishes on acidulation with sulphuric acid.

6. Certain differences are noted between the properties of the iodomercurates of the alkaloids and those of the proteins investigated.

7. Factors which may influence the sensitivity of the potassium mercuric iodide reagents with alkaloids are discussed, and the literature regarding their use as precipitating reagents for alkaloids is reviewed.

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VEHICLES FOR MEDICINES.*

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VI. SYRUP OF CINNAMON.

Syrup of cinnamon has been recommended as an "almost specific" vehicle for salicylates. As the syrup of cinnamon has a brown color, its use would coincide

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