to myself, as well as a privilege that I enjoy, I would like to add that Dr. Gordin uses the word "adsorption," as explaining the alkaloidal phenomena. Possibly he has accepted the word as employed by me in corresponding with him, and possibly he has made a scientific investigation to prove that it is altogether adsorption, or contact action, and not a chemical combination, after the manner of the usual alkaloidal reagents. Be this as it may, I wish to assume the responsibility of error of application, in case the doctor has used the word as taken from myself, and has thus been lead into accepting that view of the subject without personal investigation. Should it be shown by future experimentation that there is a chemical reaction other than adsorption, he, if the fault be mine, should be absolved from all responsibility therein.

Let me again express my deep regret that Dr. Gordin and Mr. Kaplin are not here to-day, to make a personal presentation of this paper to the Society, and let me again express my personal appreciation of the honor that has been extended me by the personal request that I read to the Society this contribution.

NOTE ON COMPARATIVE ADSORPTION OF DIFFERENT SUBSTANCES BY LLOYD'S REAGENT, ANIMAL CHARCOAL AND ALUMINUM HYDROXIDE.

H. M. GORDIN AND JAY KAPLAN.

Prof. John Uri Lloyd, in a private communication, informed me that he has discovered a reagent which quickly and completely adsorbs alkaloids from the aqueous solutions of their salts. The reagent is a natural aluminum silicate treated by a special method which he has patented in this country and will be patented abroad. Providing me with a liberal supply of the reagent, he asked me to verify his statement about the efficiency of the reagent for the complete removal of alkaloids, and gave me permission to institute upon the reagent any other set of experiments I might consider advisable. Since animal charcoal and freshly precipitated aluminum hydroxide are very much used for the removal of various substances from solution, I set up a series of experiments upon these two adsorbents along with Lloyd's reagent.

The results of my experiments, tabulated in the tables at the end of this note, may be summarized as follows:

1. The reagent resembles animal charcoal in possessing the power of adsorbing alkaloids, glucosides, bitter principles and coloring matter. While in the scope of adsorbable substances charcoal most probably excels Lloyd's reagent, in velocity of adsorption of alkaloids, the reagent by far surpasses charcoal. The complete removal of alkaloids by means of charcoal usually requires digestion with continuous shaking for several hours, while the adsorption by Lloyd's reagent is complete within a few minutes.

2. The removal of alkaloids by either the reagent or charcoal is not influenced by the presence of free acid in the solution. Even alkaloids which in the free

condition are soluble in water, such as colchicine and caffeine, can be completely adsorbed either by charcoal or Lloyd's reagent.

3. Aluminum hydroxide, so effective in the removal of acid dyes with which it forms lakes, has very little adsorptive power for alkaloids, glucosides, and bitter principles.

4. The amount of reagent or purified animal charcoal required for the complete removal of alkaloids differs with the nature of the latter, and in the case of charcoal the removal is not complete unless the digestion and shaking of the mixture lasts a certain length of time.

5. Sodium chloride is not adsorbed by Lloyd's reagent.

6. Both the reagent and charcoal adsorb acids and alkalies.

The experiments on alkaloids were carried out as follows: Solutions of alkaloidal salts or of alkaloids in acidified water were shaken with such quantities of reagent or purified animal charcoal and for such periods of time as were found by preliminary experiments to be in all cases sufficient for the complete removal of the alkaloids. The solutions were then filtered, and the acid or acidified filtrates tested with Mayer's and Wagner's reagents.

Berberine was also tested for by picric acid which is extremely delicate for this alkaloid, and for isocalycanthine the very sensitive test with gold chloride and sodium carbonate was used in addition to Mayer's and Wagner's reagents.

In working with aluminum hydroxide a comparatively large amount of aluminum sulphate was added to solutions of alkaloidal salts, and the liquids made strongly alkaline with ammonia. After shaking for some time, the liquids were filtered, and the filtrates tested as above.

In testing for the adsorption of salicin, amygdalin and aloin, the filtrates were examined by evaporating aliquot portions to dryness and weighing the residues.

In the experiments with sodium chloride the amount of the latter in the filtrate was determined by titration with standard silver nitrate.

In the experiments on the adsorption of acid and alkali the amounts of these in aliquot portions of the filtrates were determined by titration.

Another series of experiments were made in order to determine whether it would be possible to make use of either charcoal or Lloyd's reagent for the complete removal of an alkaloidal salt in presence of free acid, together with a definite amount of this acid. If this were possible, we would have here a convenient method for the quantitative determination of alkaloids. All we would have to do would be to dissolve the given alkaloid in an excess of standard acid, remove the alkaloidal salt so produced together with a definite amount of the free acid by means of the adsorbent, and then titrate the excess of acid remaining in solution. Experiments showed, however, that both Lloyd's reagent and charcoal adsorb such amounts of free acids as are entirely independent of the amount of alkaloid taken. The acid adsorbed varies with the concentration of acid, alkaloid and amount of adsorbent used.

Attempts to make the method workable by standardizing the acids against known amounts of the alkaloids failed to give concordant results. Hence the expectations in this respect were not realized.

Table IV at the end of this article is taken from Lloyd's private communication.

TABLE I.

Adsorption of different substances by Lloyd's Reagent, Purified Animal Charcoal and Freshly Precipitated Aluminum Hydroxide.

Substance.	Amount.	Concentration.	Reagent Used.	Time shaken.	Wagner's reagent.	Mayer's reagent.	Special Considerations.	Conclusion.
Caffeine	.0945 gm.	15 cc.	2.5 gm. Lloyd's reagent	3 min.	no ppt.			
Caffeine	.0945 gm.	15 cc.	2 gm. charcoal	3 hrs.	no ppt.			
Caffeine	.035 gm.	10 cc.	10 gm. $Al_2(SO_4)_3+NH_3$	15 min.	heavy ppt.			
Colchicine	.0840 gm.	15 cc.	2.5 gm. Lloyd's reagent	3 min.	no ppt.	no ppt.		
Colchicine	.0840 gm.	15 cc.	2 gm. charcoal	3 hrs.	no ppt.	no ppt.		
Strychnine Sulphate	.0831 gm.	10 cc.	2 gm. charcoal	3 hrs.	no ppt.	no ppt.		
Strychnine Sulphate	.0321 gm.	10 cc.	6 gm. $Al_2(SO_4)_3+NH_3$	15 min.	no ppt.	no ppt.		
Berberine Sulphate.	.0333 gm.	20 cc.	5 gm. Lloyd's reagent	5 min.	no ppt.	no ppt.	no test with Picric acid	
Berberine Sulphate.	.0333 gm.	10 cc.	10 gm. $Al_2(SO_4)_3+NH_3$	10 min.	heavy ppt.	heavy ppt.	filtrate still yellow	adsorption very incomplete
Morphine Sulphate.	.0520 gm.	10 cc.	2 gm. charcoal	3 hrs.	no ppt.	no ppt.		
Atropine Sulphate..	.0575 gm.	10 cc.	2 gm. charcoal	3 hrs.	no ppt.	no ppt.		
Brucine Sulphate...	.0415 gm.	10 cc.	2 gm. charcoal	3 hrs.	no ppt.	no ppt.		
Aloin	.0418 gm.	10 cc.	5 gm. Lloyd's reagent	5 min.			Aloin present .010 gm.	adsorption incomplete
Aloin	.0418 gm.	10 cc.	10 gm. $Al_2(SO_4)_3+NH_3$	5 min.			filtrate yellow and bitter	adsorption very incomplete
Aloin	.0418 gm.	20 cc.	4 gm. charcoal	3 hrs.			colorless and tasteless	adsorption complete
Salicin	.0577 gm.	20 cc.	5 gm. Lloyd's reagent	10 min.			filtrate contained .0213 gm. Salicin	adsorption incomplete
Salicin	.0577 gm.	10 cc.	10 gm. $Al_2(SO_4)_3+NH_3$	15 min.			filtrate intensely bitter	adsorption very incomplete
Salicin	.0577 gm.	20 cc.	4 gm. charcoal	3 hrs.			filtrate tasteless	adsorption complete
Isocalycanthine	.0655 gm.	15 cc.	3 gm. Lloyd's reagent	3 min.	no ppt.	no ppt.	no result upon adding $Na_2CO_3+AuCl_3$	adsorption complete
Isocalycanthine	.0655 gm.	15 cc.	3 gm. charcoal	3 hrs.	no ppt.	no ppt.	no result upon adding $Na_2CO_3+AuCl_3$	adsorption complete
Amygdalin	.2786 gm.	20 cc.	3 gm. Lloyd's reagent	5 min.			residue weighed .0613 gm.	adsorption incomplete
Indigo	.1014 gm.	20 cc.	5 gm. Lloyd's reagent	15 min.			filtrate colorless	adsorption complete
Indigo	.1014 gm.	20 cc.	10 gm. $Al_2(SO_4)_3+NH_3$	15 min.			filtrate colorless	adsorption complete
Indigo	.1014 gm.	20 cc.	4 gm. charcoal	3 hrs.			filtrate colorless	adsorption complete
Sodium chloride....	2.5 gm.	100 cc.	5 gm. Lloyd's reagent	5 min.			titrated with $AgNO_3$	no salt adsorbed

TABLE II.

Adsorption of Acid and Alkali.

Substance.	Reagent.	Time of shaking.	Amount of substance adsorbed.
50 cc. N/10 KOH+50 cc. H_2O.....	3 gm. Lloyd's reagent	5 minutes	8.91 cc. of N/10 KOH
50 cc. NH_3 sol. 0.2%+50 cc. H_2O..	3 gm. Lloyd's reagent	5 minutes	2.82 cc. of NH_3O.2%
30 cc. N/10 H_2SO_4+50 cc. H_2O....	3 gm. Lloyd's reagent	3 hours	7.8 cc. N/10 H_2SO_4
50 cc. N/10 HCl+50 cc. H_2O.....	3 gm. Lloyd's reagent	3 hours	12.61 cc. N/10 HCl
30 cc. N/10 H_2SO_4+50 cc. H_2O....	3 gm. charcoal	3 hours	6.79 cc. of N/10 H_2SO_4
50 cc. N/10 H_2SO_4+50 cc. H_2O....	3 gm. charcoal	3 hours	11.74 cc. N/10 H_2SO_4
50 cc N/10 HCl+50 cc. H_2O.....	3 gm. charcoal	3 hours	6.6 cc. of N/10 HCl

TABLE III.

Relation Between Alkaloid and Acid Adsorbed.

Alkaloid.	Acid.	Reagent.	Time shaken.	Amount of acid found to be in combination with alkaloid.	Conclusion.
.2506 gm. Morphine	N/10 H_2SO_4	7 gm. Lloyd's reagent	3 min.	3.48 cc. N/10 acid	No def. relation
.1002 gm. Morphine	N/10 H_2SO_4	7 gm. Lloyd's reagent	3 min.	.817 cc. N/10 acid	
.250 gm. Morphine	N/10 H_2SO_4	10 gm. charcoal	3 hrs.	2.342 cc. N/10 acid	No def. relation
.1002 gm. Morphine	N/10 H_2SO_4	10 gm. charcoal	3 hrs.	1.290 cc. N/10 acid	

TABLE IV.

(Lloyd's.)

Amounts of the reagent required for the complete removal of different alkaloids.

1 gm. Cocaine Hydrochlorate requires.....14 gm. of the reagent
1 gm. Strychnine Sulphate requires.....10 gm. of the reagent
1 gm. Morphine Sulphate requires..... 6 gm. of the reagent
1 gm. Brucine Sulphate requires..... 8 gm. of the reagent
1 gm. Codeine Sulphate requires..... 6 gm. of the reagent
1 gm. Cinchonine Sulphate requires.....10 gm. of the reagent
1 gm. Cinchonidine Sulphate requires.....11 gm. of the reagent
1 gm. Atropine Sulphate requires..... 8 gm. of the reagent
1 gm. Quinine Bisulphate (Neutral Solution).....10 gm. of the reagent
1 gm. Quinine Bisulphate (Acid Solution).....12 gm. of the reagent

NORTHWESTERN UNIVERSITY SCHOOL OF PHARMACY, Chicago, Ill., June 24, 1912.