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I hereby recommend that the thesis prepared under my supervision by Paul C Chang.

entitled Some Studies on the Mechanism of Vegetable Tanning

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Fred O'Flaherty

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SOME STUDIES ON THE MECHANISM OF VEGETABLE TANNAGE

A Thesis

by

Paul Chuan Chang

Presented to the Faculty

of the

University of Cincinnati

in fulfillment of part of the requirements for the

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SOME STUDIES ON THE MECHANISM OF VEGETABLE TANNAGE

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A. Introduction and History

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SOME STUDIES ON THE MECHANISM OF VEGETABLE TANNAGE

A. Introduction and History

I. Introduction

In the past few decades, extensive work has been performed on the study of the fixation of vegetable tannins by proteins, but due to the complexity of the structure of both the proteins and the tannins, the actual mechanism of vegetable tannage is by no means completely understood. Two main theories, namely, chemical and physical, have been advanced by previous workers to explain the process of vegetable tannage. With the recent progress of colloid chemistry, protein chemistry, and the application of the x-ray in the investigation of the structure of the raw versus tanned hide fibers, our knowledge of tanning has been greatly enhanced. Even so, further work must be done on this complicated problem before a definite statement can be made as to what actually constitutes tanning.

A. Introduction and History

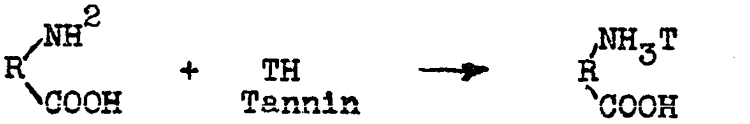
II. Purpose

The purpose of this study was to investigate the quantitative sorption of some tanning agents whose chemical structure is known by commercially prepared hide powder under various specified conditions.

A. Introduction and History

III. Historical Review

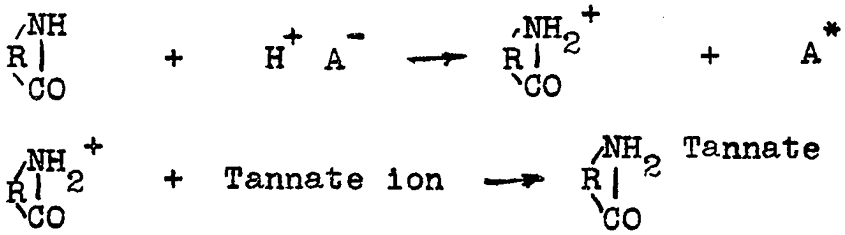
Armand Sequin(1) in 1795, observing the precipitation of glue from a solution by the addition of a tanning liquor, postulated that a salt formation took place between the basic amino groups of the glue and the acidic tannin molecules as follows:



$$\mathrm{R}\begin{matrix}\diagup\mathrm{NH^2}\\ \diagdown\mathrm{COOH}\end{matrix} + \underset{\text{Tannin}}{\mathrm{TH}} \longrightarrow \mathrm{R}\begin{matrix}\diagup\mathrm{NH_3T}\\ \diagdown\mathrm{COOH}\end{matrix}$$

Vegetable Tanned
Leather

In 1917, Procter and Wilson(2) formulated an electrical charge neutralization theory based upon their investigations of the physical theory of proteins. According to their neutralization theory, the tannin is present as negatively charged colloid particles in water. For the tannin to precipitate the proteins, the proteins must first combine with the acid present in a slightly acidic solution to form a positively charged colloid. These oppositely charged colloids then unite and cause co-precipitation. The degree of activity of this reaction is governed by the hydrogen ion concentration of the solution. The reactions taking place, according to Wilson(3) are as follows:



$$\mathrm{R}\begin{matrix}\diagup\mathrm{NH}\\ |\\ \diagdown\mathrm{CO}\end{matrix} + \mathrm{H^+\,A^-} \longrightarrow \mathrm{R}\begin{matrix}\diagup\mathrm{NH_2^+}\\ |\\ \diagdown\mathrm{CO}\end{matrix} + \mathrm{A^*}$$

$$\mathrm{R}\begin{matrix}\diagup\mathrm{NH_2^+}\\ |\\ \diagdown\mathrm{CO}\end{matrix} + \text{Tannate ion} \longrightarrow \mathrm{R}\begin{matrix}\diagup\mathrm{NH_2}\ \text{Tannate}\\ |\\ \diagdown\mathrm{CO}\end{matrix}$$

Vegetable Tanned
Leather

Stiasny(4) claims in his recent paper "The Development in the Theory of Tanning", that the physical theory of vegetable tanning still predominates the chemical theory. He states that the physical concept explains more satisfactorily the complex nature of vegetable tanning than does the chemical concept. Stiasny's adsorption theory(5), which is a modification of Friedrich Knopp's(6) original theory, is "That tanning consists primarily of the adsorption of a semicolloidal substance and that the irreversibility of the tannins on skin is caused by the secondary change taken place after the adsorption". His concept is based on the information known about surface phenomena and suggests that the same law governs the take-up of tannin by hide as the adsorption of gases or of dissolved substances by charcoal. An "adsorption curve" seems to be the characteristic proof for identifying any of these phenomena.

The fixation of chromium salts by skin has been quantitatively measured by McLaughlin and his co-workers(7). These investigators claim that the adsorption isotherm of Freundlich can be applied to explain the practical chrome tanning, and that the reaction between the skin and various concentrations of chromium salt does follow the adsorption phenomenon as formulated by Freundlich.

Recent developments in the field of protein chemistry, especially in regard to the structure of the protein molecules, have been used to explain the above theories. One explanation given is that some of the active side chains adjacent to the polypeptide chains are greatly responsible for the chemical activity of the protein molecules. These active groups contain Zwitterions and take up water to cause hydration of the protein molecules. As tannins cause a dehydration of the collagen by elimination of the polar groups, Meunier(8) and Jordan Lloyd(9) suggest that tanning may be defined as a conversion of the lyophilic collagen into a lyophobic substance. That tanning takes place at the active centers of the side chains is claimed by Lloyd as follows: "The negatively charged center of the carboxyl groups of the collagen is inactivated by the acidic character of the tanning liquor and the amino groups which form positively charged centers in water by chemical interaction with the tanning agent. Suppression of the positively and negatively charged centers will lead to loss of bound water by the collagen." The dehydration effect caused by the tannins on the active centers of collagen causes the resulting leather fibers to be more stable to water. Lloyd also states that the polypeptide backbone of the collagen is protected against the action of proteolytic enzymes, suggesting that the hydroxyl groups of the vegetable tannins may also interact with the imino groups of the polypeptide links.

Some valuable information has been obtained by the recent investigations of the combination between collagen and tannin by means of the x-ray. This method of study of the structure of tanned leather has been used by Katz and Gerngross(10), Thuau(11), Jordan Lloyd(9), and Highberger and Kersten(12). They agree that the x-ray pictures of vegetable tanned leather fibers show a loss of definition of interference caused by the side chain spacing. However, the interference caused by the backbone spacing, and represented by the outer ring in the x-ray picture, of oak tanned leather as given by Katz and Gerngross is weakened in intensity. Thuau compares the x-ray pattern of the tanned skin with that of raw skin, and finds that the tanned skin picture is the same as the raw skin picture plus the superimposed diagram of the tanning material. Katz and Gerngross suggest that adsorption of the tanning material on the surface of the collagen micelles possibly takes place. Thuau suggests that adsorption or some other physical fixation may take place along with any possible chemical combination. On the other hand, Lloyd found that in a very high quality English vegetable tanned leather, no great change in the outer ring (backbone spacing interference ring) took place. In a sample of leather of poor quality, the x-ray picture showed a loss of the outermost ring. Highberger and Kersten, by examining commercial vegetable tanned leather, found a slight change of the backbone spacing ring. When they examined the pattern of purified collagen powders tanned with tannic acid, they found that the backbone spacing ring had entirely disappeared upon the fixation of 0.739 grams of tannic acid per gram of collagen.

B. Experimental

I. Materials and Methods

(a) Tanning Materials

Two Tanning materials were used in these experiments, one being Mallinckrodt Chemical Company tannic acid, analytical reagent, the other the tannin of Chinese nut galls purified from the raw material by the method outlined by Russell(13). In accordance with Russell's method, the nut galls were crushed and extracted with cold water by the counter current method. The extraction was carried out as rapidly as possible to prevent any fermention of the tanning liquor. The concentrated extract was salted out with concentrated Na Cl, discarding the supernatant. The precipitate was dried in a vacuum at 60°c. After drying, the material was pulverized and extracted in a Soxhlet extractor with acetone. The acetone extract was evaporated on a water bath to a viscous state and then transferred to a vacuum oven to dry. The dried material was ground in a mortar, washed five times with ethyl either, and re-dried in the vacuum. The resulting tannin was a light yellow powder, readily and completely soluble in water, alcohol, and acetone. The tannin was stored in a tightly stoppered bottle in the dark until used.

(b) Hide Powder

Standard Hide Powder, prepared according to the official regulations of the American Leather Chemical Association, was purchased from the Standard Hide Powder Company and used in these experiments. All the samples used were from one lot of hide powder.

(c) Method of Analysis of Tannic Acid

The Lowenthal(14) oxidation method, originally proposed by Lowenthal in 1860, and subsequently improved by Procter, gives excellent results with solutions of pure tannic acid, and is convenient to use when a great many analyses have to be performed.

The solutions required are:

1) Indigo carmine solution
2) Potassium permanganate solution
3) Standard tannic acid solution

1. Indigo carmine solution: Five grams of indigo carmine were weighed and made into a paste with a little water. Fifty grams of concentrated sulfuric acid c.p. were added to dissolve the indigo carmine paste and diluted to one liter with distilled water. This dye solution was then filtered.

2. Potassium permanganate solution: 0.5 grams of potassium permanganate c.p. per liter. This solution was freshly prepared for every experiment.

3. Standard tannic acid solution: Two grams of tannic acid per liter. This solution was prepared fresh for each experiment.

The titration was performed as follows: Twenty-five mls. of indigo carmine solution and seven hundred mls. of distilled water were measured into a casserole of one liter capacity. This was titrated against the permanganate solution, the end point being a change from blue to straw yellow, and constituted the blank titration. Twenty-five mls. of tannic acid solution were added to the indigo carmine distilled water solution and titrated with permanganate. After correction for the blank, the tannic acid equivalent of one ml. of permanganate solution could be obtained. The titrations checked very well.

B. Experimental

II. The Effect of the Concentration on the Sorption of Tannic Acid by Hide Powder.

Various concentrations of tannic acid, ranging from 0.2 grams to 2.5 grams per liter, were prepared. To 200 mls. of a given concentration was added 2 grams of hide powder, and the total shaken for twenty-four hours on a shaking machine. At the end of this time, the samples were filtered and the filtrate analyzed for tannic acid by the Lowenthal method. The amount of tannic acid taken up by the hide powder was calculated by the difference method.

This procedure proved to be unsatisfactory for several reasons, namely, (1) the dry hide powder took water from the tanning solution, thereby giving a higher concentration of tannin; (2) the filter paper may adsorb some of the tannin; (3) the pH values of the solutions were not equal at the start of the experiment; and (4) the initial pH and the equilibrium pH of a given solution were not the same. Consequently, the procedure was altered to eliminate these variables as much as possible. To prevent negative adsorption, the hide powder was soaked for twenty-four hours in M/10 phosphate buffer, and the equilibrium pH of the buffer determined. This wetted hide powder was drained, the excess solution squeezed out by hand, thoroughly mixed, and weighed to determine approximately the water content. An estimated amount of wet hide powder, corresponding to approximately two grams of dry hide powder was placed in tared bottles and quicly stoppered. These bottles containing the hide powder were weighed on an analytical balance, and the weight of the wet hide powder per sample determined. A proportional amount, based upon 200 ml. of solution to 2 grams of dry hide powder, of the tannic acid, which was buffered with M/10 phosphate to the equilibrium pH stated above, was then added and the samples shaken for a given period of time. As the method of moisture determination was not accurate, only intra and not inter comparison between the data should be made, except in those instances where the ratio of dry hide powder to mls. of solution is the same or very nearly the same. A more accurate determination of the moisture content of the hide powder of each series was made by drying a weighed sample in the vacuum oven and re-weighing.

After shaking, the samples were allowed to stand for an hour to allow the hide powder to settle. The supernatant liquor was carefully decanted and used for analysis.

The results of the sorption of tannic acid when the pH was maintained at 4.78 are shown in Table I. The moisture content of the wet hide powder in this series was 71.6 per cent, and the ratio of solution to dry hide powder was 112 to 1. In calculating the total amount of tannic acid remaining in solution, the water introduced with the hide powder was considered as free water capable of diluting the tannic acid. Computations were also made considering with water as bound water incapable of diluting the tannic acid, but it was found that unless the moisture content of the hide powder was excessively high, the difference in results was negligible.

The pH values of the tanning solutions before and after tanning were all 4.78 as measured with the glass electrode.

B. Experimental

III. The Effect of the pH Value on the Sorption of Tannic Acid and Tannin by Hide Powder.

In order to study the effect of the acidity of the solution on the sorption of tannic acid by hide powder, series of experiments were carried out at maintained pH 3.14, 3.60, 4.78 (as shown in Table I), and 5.6, respectively. The concentrations used were the same as shown in Table I. The procedure used was the same as described above. The results of these experiments are shown in Tables I, II, III, IV, and graphically in Figures III, IV, VI, VII, VIII, and IX.

The procedures were repeated, using the purified tannin from nut galls (penta-digalloyl-B-glucose). The results of these studies are given in Tables V, VI, VII, and graphically in Figures IV, VIII, and IX.

TABLE I

SORPTION OF TANNIC ACID BY HIDE POWDER AT pH 4.78.

No.	Original conc. gms. Tannic acid per 1 gm. Hide powder	Final conc. gms. Tannic acid per 1 gm. Hide powder	Equilibrium conc. gms. Tannic acid per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.2190	.0245	.0185	.1945	.0925
2.	.4420	.0465	.0429	.3955	.1070
3.	.6580	.0920	.0820	.5660	.1450
4.	.8790	.1797	.1600	.6993	.2280
5.	1.1000	.3030	.2700	.7970	.3390
6.	1.3400	.4560	.4060	.8840	.4520
7.	1.5400	.6340	.5640	.9060	.6200
8.	1.7650	.7960	.7060	.9690	.7320
9.	2.2100	1.1500	1.0250	1.0600	1.0300
10.	2.7500	1.6100	1.4340	1.1400	1.2500

TABLE II

SORPTION OF TANNIC ACID BY HIDE POWDER AT pH 3.14.

No.	Original conc. gms. Tannic acid per 1 gm. Hide powder	Final conc. gms. Tannic acid per 1 gm. Hide powder	Equilibrium conc. gms. Tannic acid per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.2052	.0299	.0271	.1753	.1544
2.	.4090	.0587	.0520	.3505	.1483
3.	.6140	.1113	.1000	.5022	.1990
4.	.8060	.1660	.1510	.6400	.2560
5.	1.0210	.2590	.2230	.7620	.2920
6.	1.1750	.3095	.2890	.8655	.3340
7.	1.3635	.4410	.4140	.9225	.4470
8.	1.6040	.5590	.5110	1.0450	.4880
9.	1.8300	.7000	.6520	1.1300	.5590
10.	2.0100	.8280	.7530	1.1820	.6380
11.	2.5600	1.1710	1.0500	1.3890	.7550

TABLE III

SORPTION OF TANNIC ACID BY HIDE POWDER AT pH 3.60

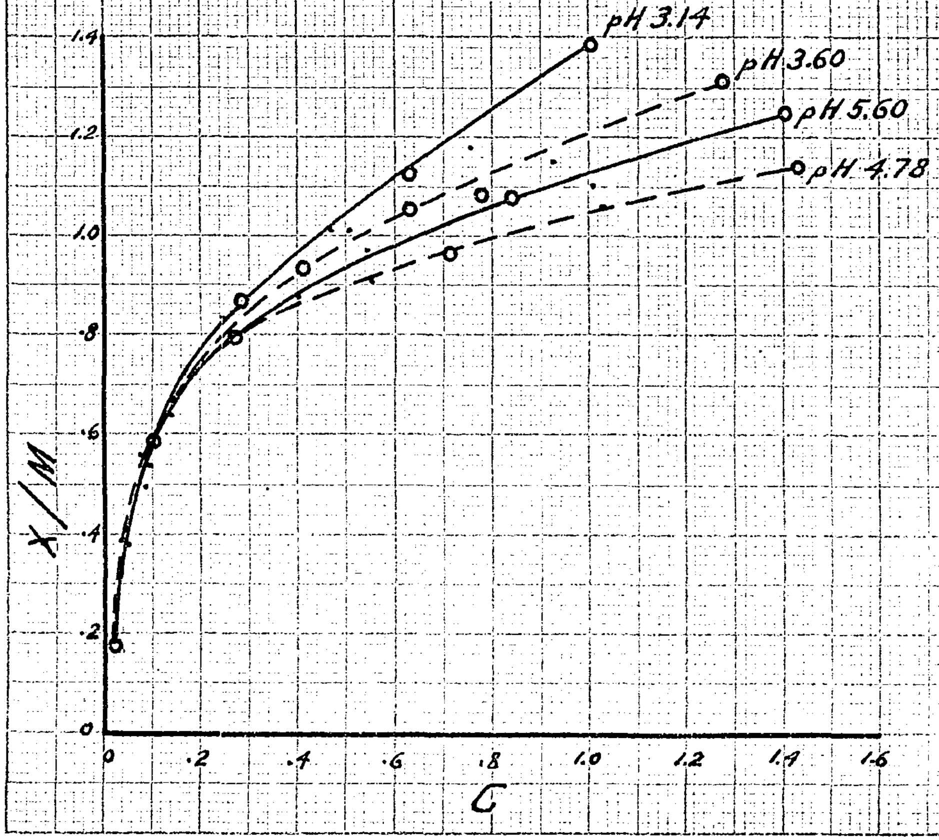
No.	Original conc. gms. Tannic acid per 1 gm. Hide powder	Final conc. gms. Tannic acid per 1 gm. Hide powder	Equilibrium conc. gms. Tannic acid per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.2260	.0312	.0266	.1948	.1360
2.	.4500	.0640	.0544	.3860	.1410
3.	.6620	.1195	.1033	.5425	.1905
4.	.8630	.1960	.1690	.6970	.2460
5.	1.1180	.2900	.2470	.8280	.2980
6.	1.3400	.4130	.2540	.9270	.2740
7.	1.5570	.5470	.4670	1.0100	.4660
8.	1.7840	.7350	.6270	1.0490	.5980
9.	2.0030	.9260	.7920	1.0770	.7350
10.	2.2280	1.0820	.9250	1.1460	.8070
11.	2.8200	1.5130	1.2770	1.3070	.9770

TABLE IV

SORPTION OF TANNIC ACID BY HIDE POWDER AT pH 5.60

No.	Original conc. gms. Tannic acid per 1 gm. Hide powder	Final conc. gms. Tannic acid per 1 gm. Hide powder	Equilibrium conc. gms. Tannic acid per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.2308	.0242	.0210	.2100	.1000
2.	.4610	.0622	.0520	.3990	.1300
3.	.6940	.1180	.1000	.5760	.1740
4.	.9200	.1890	.1680	.7310	.2300
5.	1.1550	.3560	.2830	.7990	.3560
6.	1.3850	.4770	.4020	.9080	.4420
7.	1.6200	.6450	.5350	.9750	.5500
8.	1.8560	.8070	.6780	1.0510	.6460
9.	2.0780	1.0220	.8650	1.0560	.8200
10.	2.2980	1.1970	1.0120	1.1010	.9200
11.	2.8900	1.6420	1.4180	1.2460	1.1060

14e



Sorption of Tannic Acid

by Hide Powder

at various pH

FIG. III

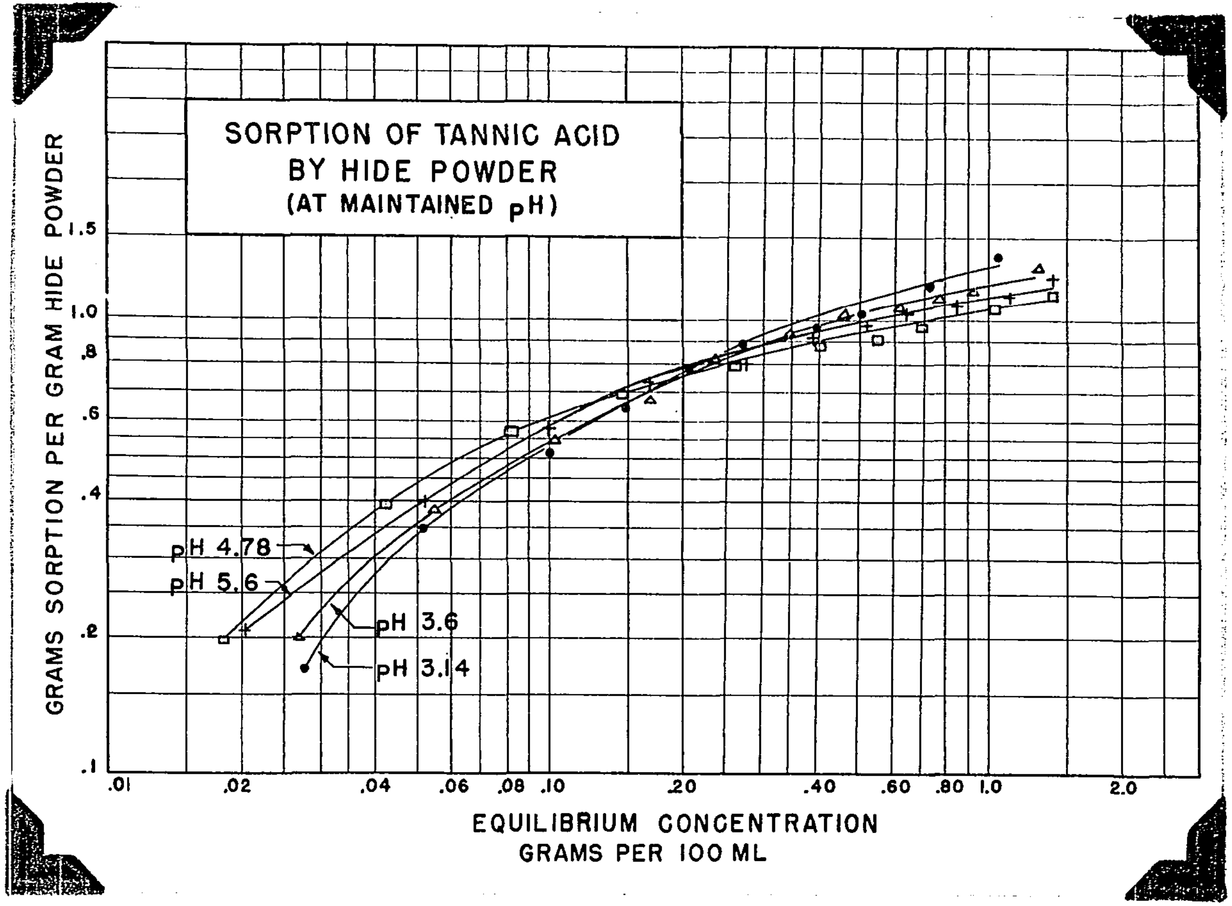

SORPTION OF TANNIC ACID
BY HIDE POWDER
(AT MAINTAINED pH)
GRAMS SORPTION PER GRAM HIDE POWDER
.1
.2
.4
.6
.8
1.0
1.5
.01
.02
.04
.06
.08
.10
.20
.40
.60
.80
1.0
2.0
EQUILIBRIUM CONCENTRATION
GRAMS PER 100 ML
pH 4.78
pH 5.6
pH 3.6
pH 3.14

Figure VI

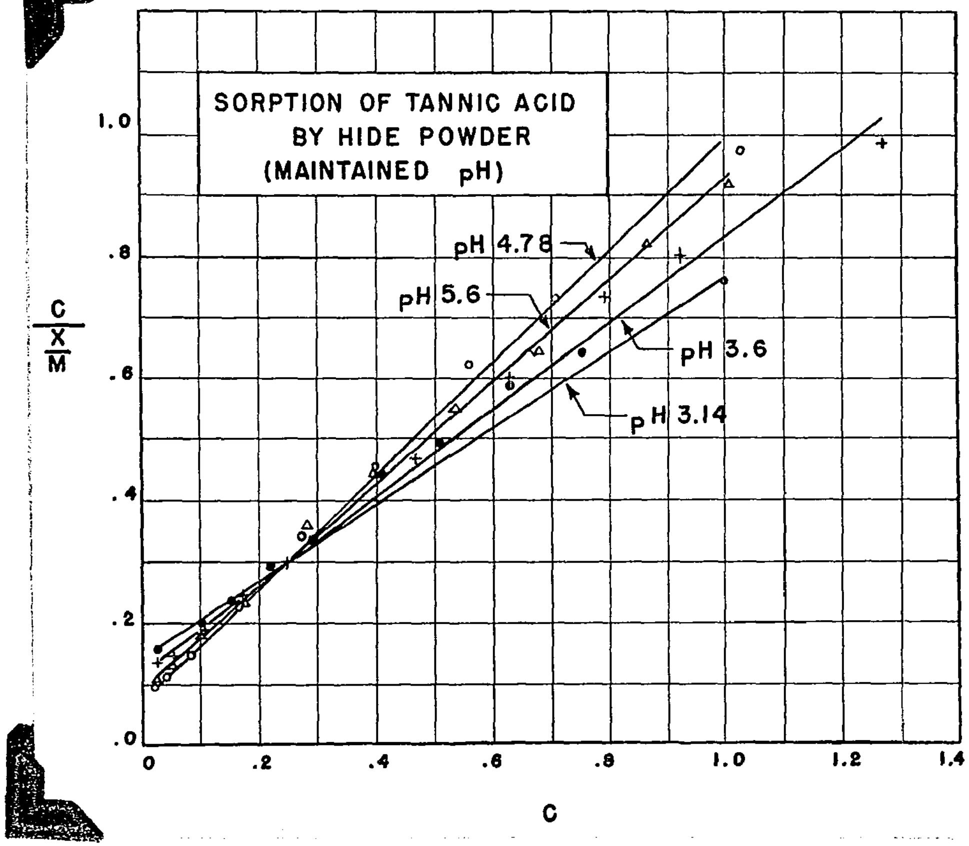

SORPTION OF TANNIC ACID
BY HIDE POWDER
(MAINTAINED pH)
pH 4.78
pH 5.6
pH 3.6
pH 3.14
C/(X/M)
1.0
.8
.6
.4
.2
.0
0
.2
.4
.6
.8
1.0
1.2
1.4
C

Figure VII

TABLE V

SORPTION OF PENTA-DIGALLOYL-β-GLUCOSE BY HIDE POWDER AT pH 2.75.

No.	Original conc. gms. Tannin per 1 gm. Hide powder	Final conc. gms. Tannin per 1 gm. Hide powder	Equilibrium conc. gms. Tannin per 100 ml solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.1990	.0189	.0182	.1801	.1050
2.	.3805	.0409	.0394	.3396	.1160
3.	.5615	.0685	.0672	.4930	.1360
4.	.7540	.1036	.1010	.6504	.1550
5.	1.1410	.2420	.2195	.8990	.2440
6.	1.5280	.4100	.3940	1.1180	.3530
7.	1.9100	.7160	.6860	1.1194	.5750
8.	2.4820	.9020	.8680	1.5800	.5500
9.	2.8550	1.2480	1.2020	1.6070	.7500
10.	3.6815	1.9800	1.9050	1.7015	1.1200

TABLE VI

SORPTION OF PENTA-DIGALLOYL-β-GLUCOSE BY HIDE POWDER AT pH 3.75

No.	Original conc. gms. Tannin per 1 gm. Hide powder	Final conc. gms. Tannin per 1 gm. Hide powder	Equilibrium conc. gms. Tannin per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.1917	.0182	.0182	.1735	.1050
2.	.4090	.0383	.0364	.3710	.0983
3.	.5880	.0650	.0627	.5230	.1200
4.	.7740	.0992	.0970	.6748	.1440
5.	1.1900	.2455	.2345	.9445	.2490
6.	1.5680	.4390	.4240	1.1290	.3760
7.	1.9760	.7330	.7030	1.2430	.5660
8.	2.4650	1.0470	.9940	1.4180	.7000
9.	2.9450	1.4300	1.3800	1.5150	.9120
10.	3.9400	2.1550	2.0700	1.7850	1.1600

TABLE VII

SORPTION OF PENTA-Digallyl-β-GLUCOSE BY HIDE POWDER ATpH 5.00

No.	Original conc. gms. Tannin per 1 gm. Hide powder	Final conc. gms Tannin per 1 gm. Hide powder	Equilibrium conc. gms. Tannin per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.1883	.0127	.0129	.1756	.0735
2.	.3750	.0349	.0355	.3401	.1040
3.	.5690	..0560	.0568	.5130	.1110
4.	.7570	.0945	.0956	.6625	.1440
5.	1.1530	.2910	.2945	.9620	.3410
6.	1.5230	.5490	.5540	.9740	.5700
7.	1.8800	.7700	.7800	1.1100	.7030
8.	2.3400	1.2530	1.2730	1.0870	1.1700
9.	2.8350	1.6500	1.6600	1.1850	1.4000
10.	3.7800	2.4880	2.5500	1.2920	1.9700

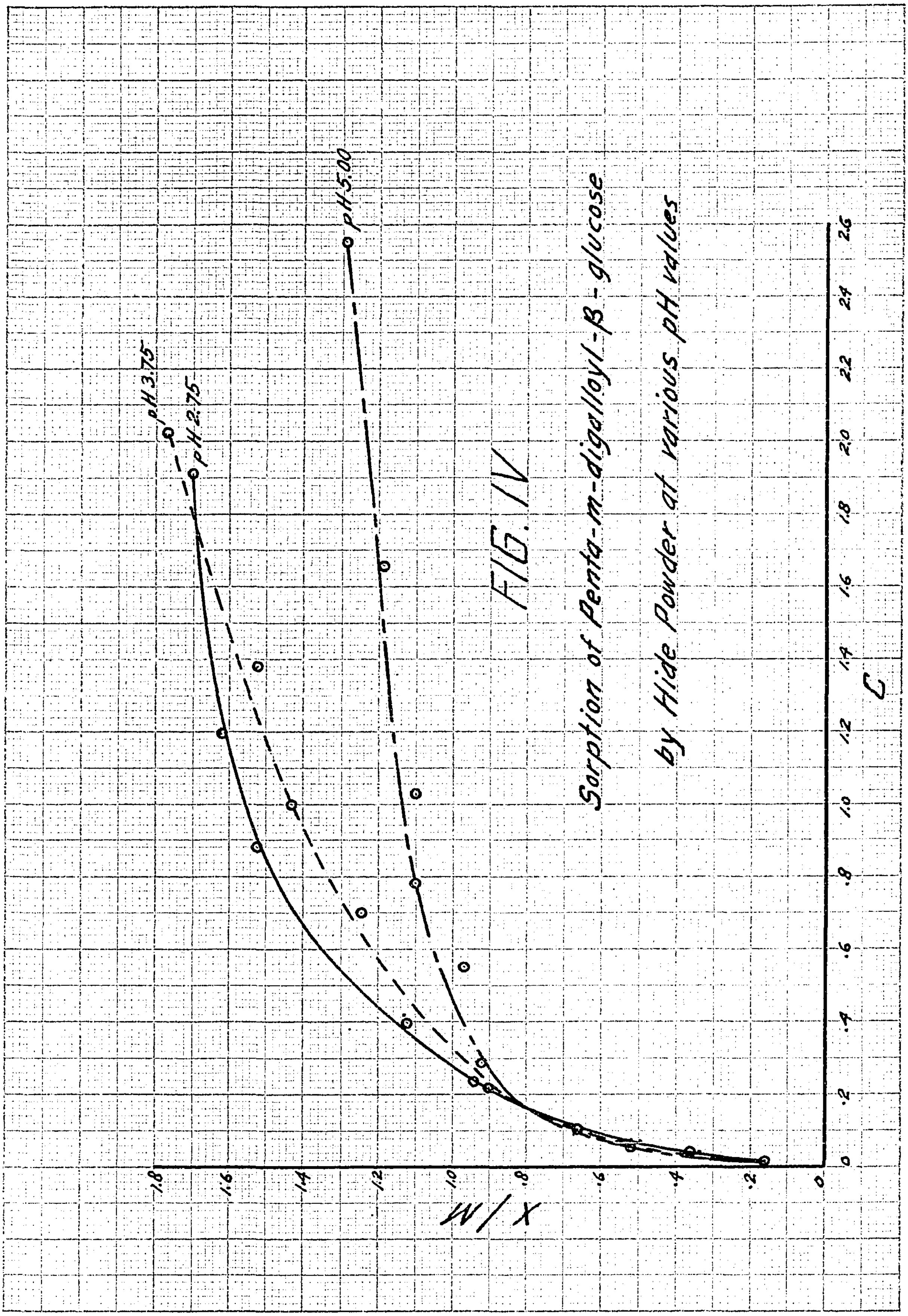


FIG. IV

Sorption of Penta-m-digalloyl-β-glucose by Hide Powder at various pH values

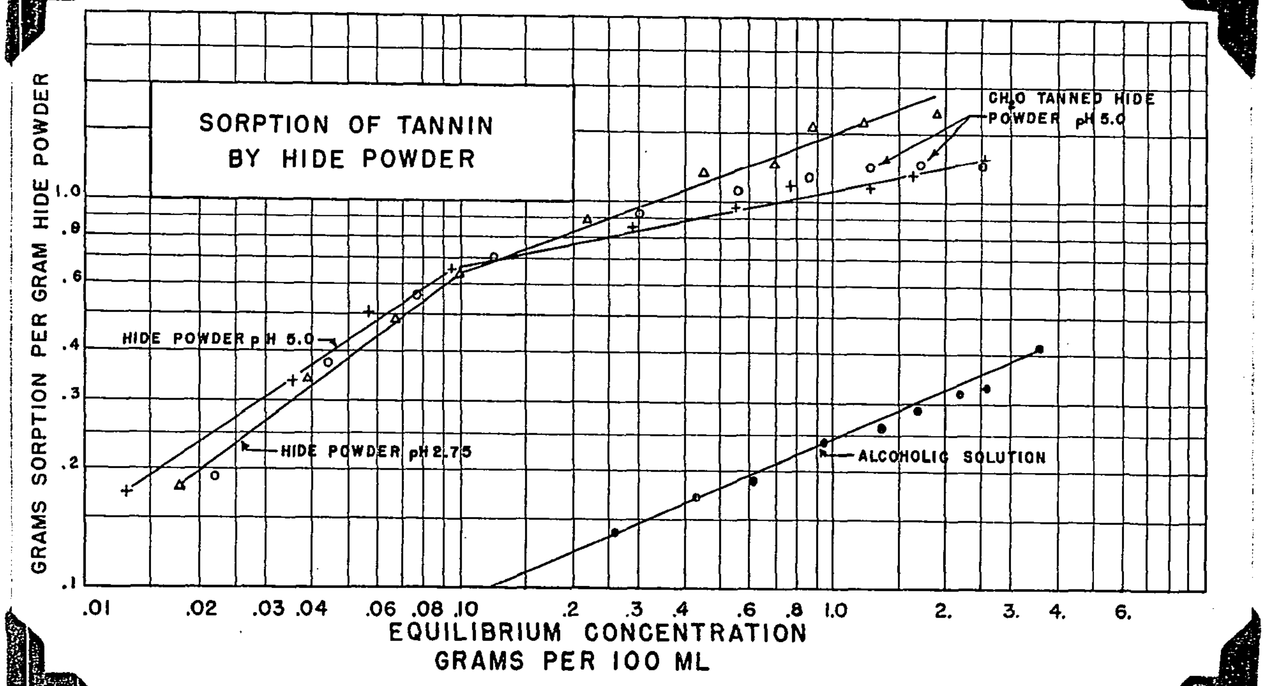

SORPTION OF TANNIN
BY HIDE POWDER
GRAMS SORPTION PER GRAM HIDE POWDER
1.0
.8
.6
.4
.3
.2
.1
.01
.02
.03
.04
.06
.08
.10
.2
.3
.4
.6
.8
1.0
2.
3.
4.
6.
EQUILIBRIUM CONCENTRATION
GRAMS PER 100 ML
HIDE POWDER pH 5.0
HIDE POWDER pH 2.75
CH2O TANNED HIDE POWDER pH 5.0
ALCOHOLIC SOLUTION

Figure VIII

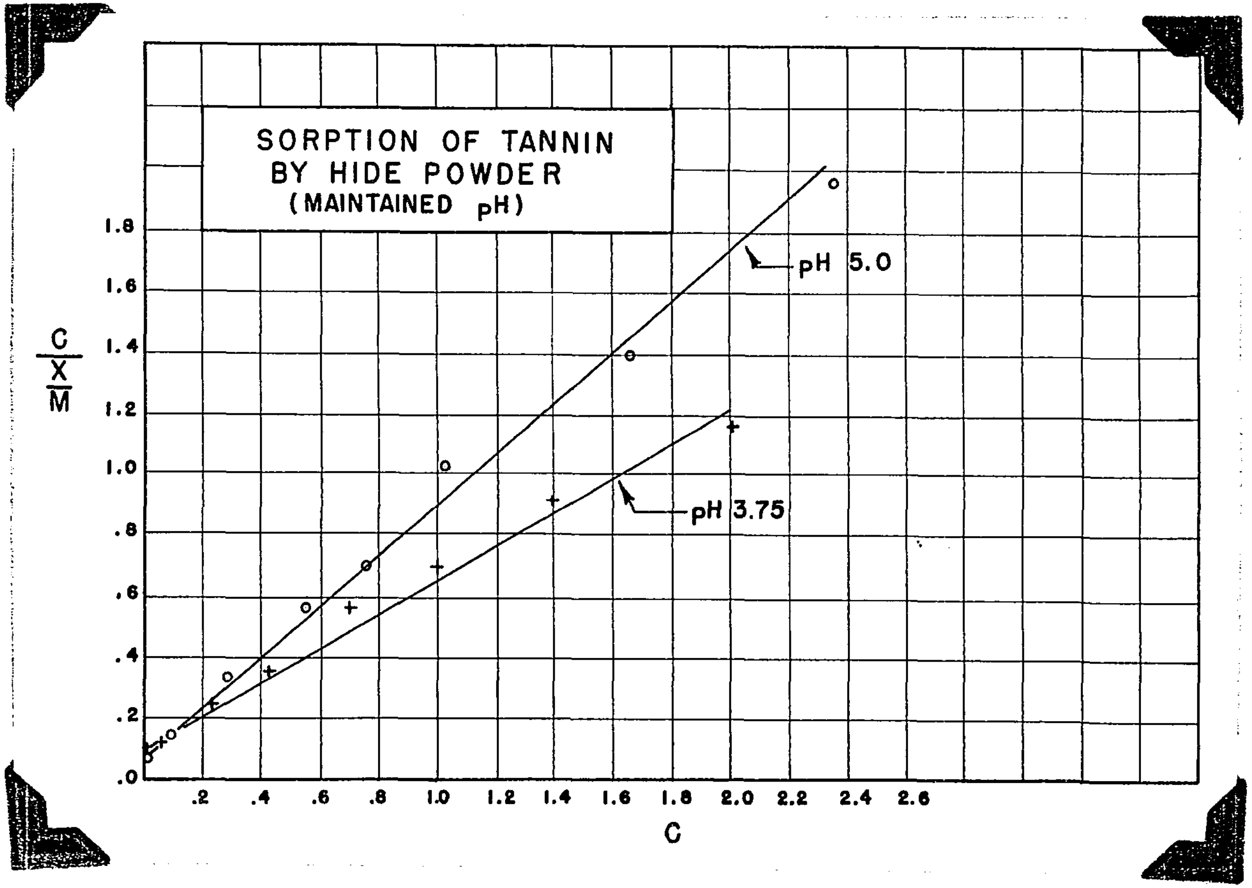

SORPTION OF TANNIN
BY HIDE POWDER
(MAINTAINED pH)
pH 5.0
pH 3.75
C/(X/M)
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
.0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
C

Figure IX

B. Experimental

IV. The Sorption of Tannic Acid and Tannin by Formaldehyde Tanned Hide Powder.

According to Highberger(20), formaldehyde combines chemically with the free un-ionized amino groups of the protein in a one to one ratio. Therefore, if the chemical theory of tanning is true, one would expect a marked decrease in the take-up of tannic acid or tannin by hide powder tanned with formaldehyde. Also, if formaldehyde tanned hide powder does combine with tannic acid or tannin, the latter must be attached to some group other than the amino group. To test for this, different series of experiments, varying the concentration of tannic acid at a maintained pH value and at different pH values were performed. In all cases, the tannic acid solutions were buffered to the equilibrium pH value of the buffered hide powder with M/10 phosphate.

The formaldehyde tanned hide powder was prepared as follows: One gram of hide powder was tanned in 100 mls. of solution containing 25 mls. of molar NaOH, 10 mls. of molar phosphoric acid, and 2.5 mls. of formaldehyde (40 per cent), for 24 hours, with occasional shaking. The alkalinity was used so that the amino groups would be un-ionized. After 24 hours, the excess formaldehyde was drained off, and the hide powder washed several times with 0.2 N Na_2SO_3. The excess Na_2SO_3 was then washed out with distilled water.

Finally, the hide powder was placed in M/10 phosphate buffer at the desired pH for 24 hours. The rest of the procedure was the same as given above.

The results of the experiments are given in Tables VIII, IX, X, and XI, and shown graphically in Figures V, X, and XI

When penta-digalloyl-B-glucose was used, the results shown in Table XV and Figure VIII were obtained.

TABLE VIII

SORPTION OF TANNIC ACID BY CH_2O TANNED HIDE POWDER AT pH 2.93

No.	Original conc. gms. Tannic acid per 1 gm. Hide powder	Final conc. gms. Tannic acid per 1 gm. Hide powder	Equilibrium conc. gms. Tannic acid per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.2201	.0301	.0267	.1900	.1400
2.	.4360	.0687	.0615	.3673	.1675
3.	.6550	.1360	.1376	.5190	.2650
4.	.8700	.2805	.2500	.5895	.4240
5.	1.1560	.4715	.3960	.6845	.5780
6.	1.3100	.6340	.5600	.6760	.8360
7.	1.5530	.8060	.7160	.6970	1.0250
8.	1.7250	1.0180	.9030	.7540	1.2300
9.	1.9600	1.2100	1.0730	.7500	1.4300
10.	2.1820	1.4150	1.2600	.7670	1.6400
11.	2.7500	1.8520	1.6470	.8980	1.8300

TABLE IX

SORPTION OF TANNIC ACID BY CH_2O TANNED HIDE POWDER AT pH 3.60

No.	Original conc. gms. Tannic acid per 1 gm. Hide powder	Final conc. gms Tannic acid per 1 gm. Hide powder	Equilibrium conc. gms. Tannic acid per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.1860	.0204	.0245	.1650	.1485
2.	.3610	.0600	.0610	.3010	.2028
3.	.5570	.1390	.1420	.4180	.3390
4.	.7610	,2780	.2780	.4830	.5760
5.	.9260	.4060	.4150	.5200	.7970
6.	1.1100	.5330	.5440	.5770	.9450
7.	1.2960	.6760	.6910	.6200	1.1160
8.	1.4180	.8250	.9540	.6430	1.4820
9.	1.6720	.9850	1.0000	.6870	1.4700
10.	1.8630	1.1580	1.1820	.7050	1.6740
11.	2.3310	1.6600	1.7020	.6650	2.5600

TABLE X

SORPTION OF TANNIC ACID BY CH_2O TANNED HIDE POWDER AT pH 4.40

No.	Original conc. gms. Tannic acid per 1 gm. Hide powder	Final conc. gms. Tannic acid per 1 gm. Hide powder	Equilibrium conc. gms. Tannic acid per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.1782	.0236	.0256	.1540	.1656
2.	.3560	.0542	.0566	.3038	.1930
3.	.5360	.1312	.1410	.4048	.3480
4.	.7160	.2360	.2560	.4800	.5330
5.	.8950	.3810	.4230	.5100	.8240
6.	1.0700	.5310	.5760	.5390	1.0700
7.	1.2800	.6970	.7350	.5830	1.2600
8.	1.4340	.8750	.9465	.5640	1.6800
9.	1.6100	1.0400	1.0950	.5700	1.9200
10.	1.7500	1.1800	1.2870	.6000	2.1400
11.	2.2420	1.5900	1.7730	.6500	2.7200

TABLE XI

SORPTION OF TANNIC ACID BY CH_2O TANNED HIDE POWDER AT pH 5.30

No.	Original conc. gms. Tannic acid per 1 gm. Hide powder	Final conc. gms. Tannic acid per 1 gm Hide powder	Equilibrium conc. gms. Tannic acid per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.2355	.0374	.0303	.1980	.1450
2.	.4710	.0851	.0691	.3859	.1790
3.	.7160	.1557	.1258	.5603	.2330
4.	.9600	.2710	.2180	.6890	.3160
5.	1.1770	.4335	.3522	.7435	.4740
6.	1.4200	.6200	.5030	.8000	.6300
7.	1.6510	.8130	.6600	.8380	.7850
8.	1.8860	.9760	.7620	.9100	.8370
9.	2.1400	1.2350	.9500	.9050	1.0500
10.	2.5600	1.4500	1.1800	.9100	1.2940
11.	2.8420	1.9900	1.6250	.8520	1.9100

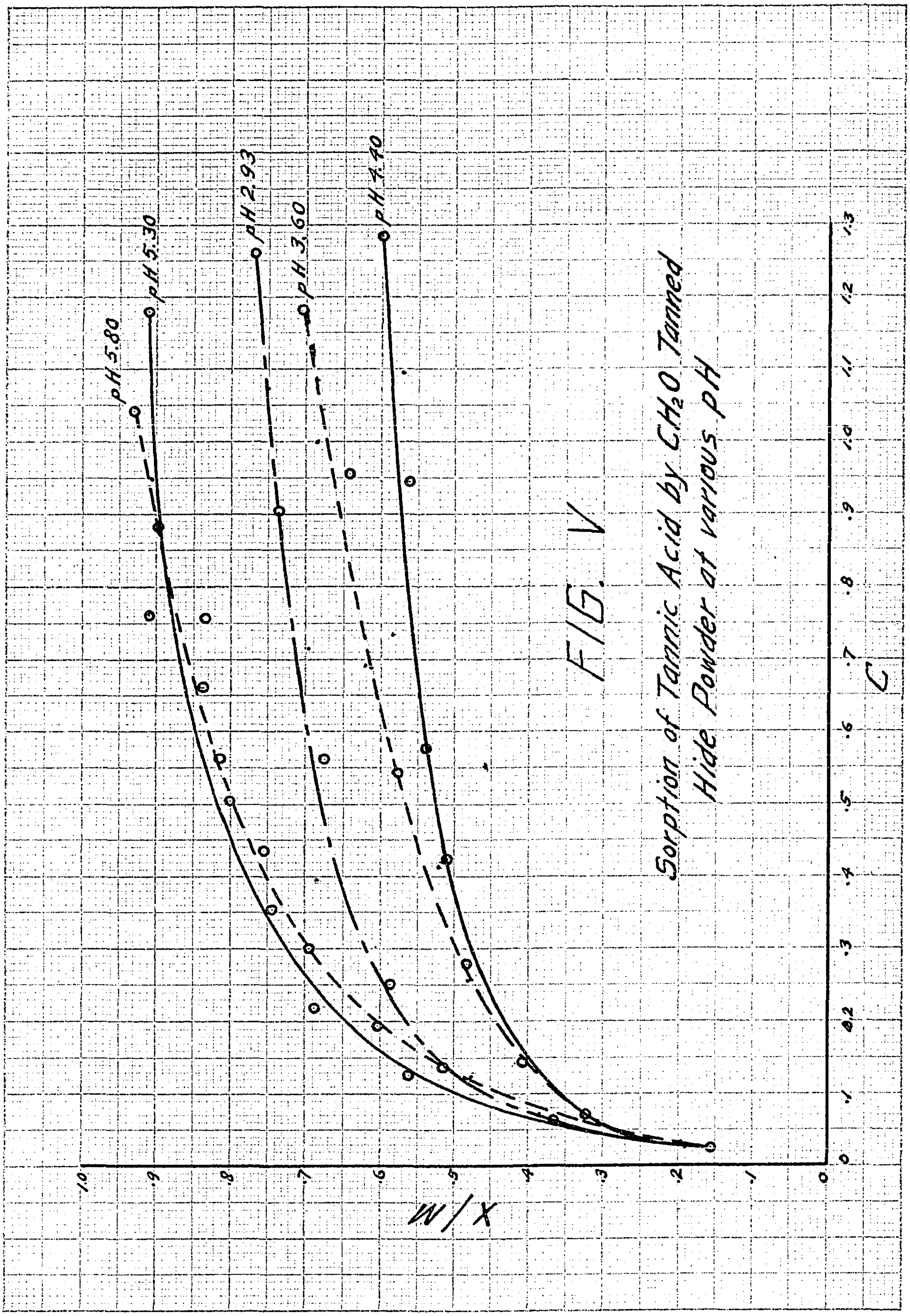


FIG. V

Sorption of Tannic Acid by CH_2O Tanned Hide Powder at various pH

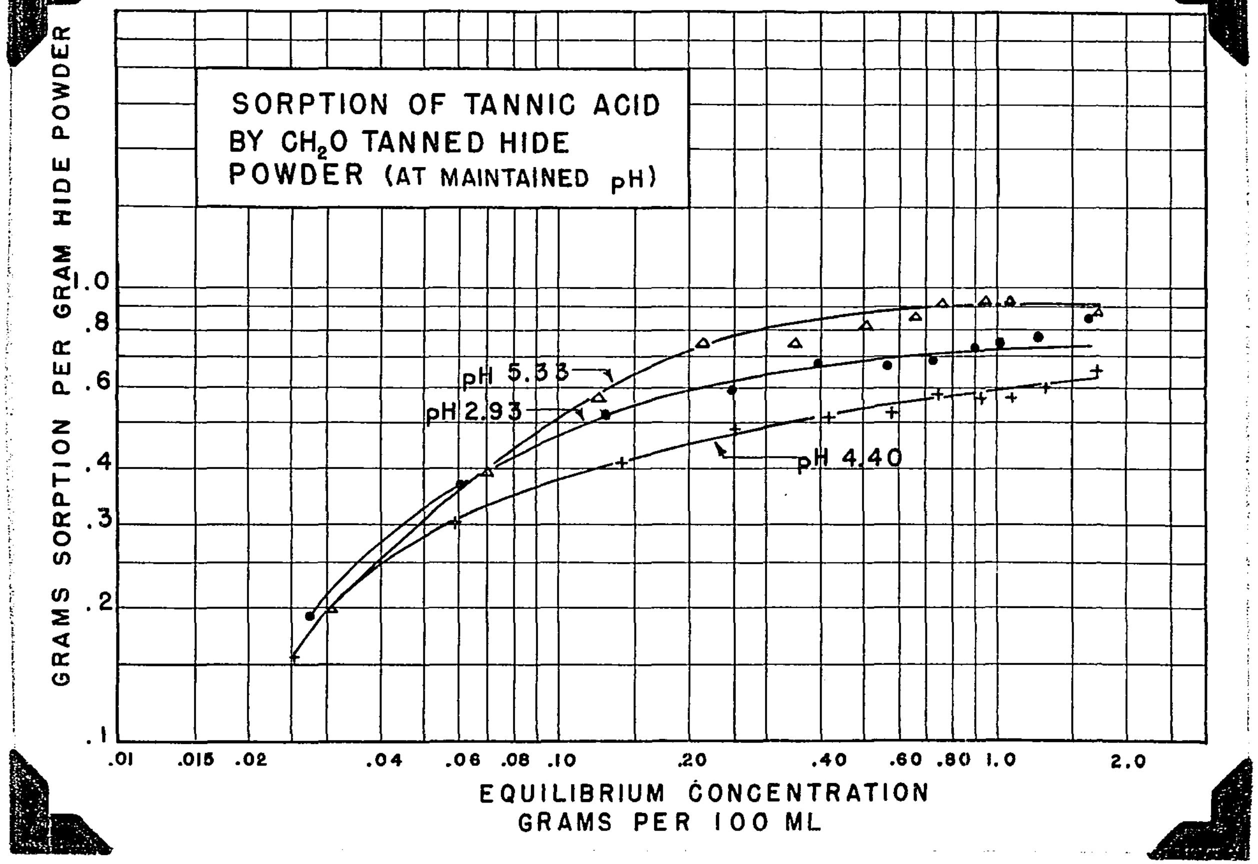

SORPTION OF TANNIC ACID
BY CH₂O TANNED HIDE
POWDER (AT MAINTAINED pH)
GRAMS SORPTION PER GRAM HIDE POWDER
1.0
.8
.6
.4
.3
.2
.1
.01
.015
.02
.04
.06
.08
.10
.20
.40
.60
.80
1.0
2.0
EQUILIBRIUM CONCENTRATION
GRAMS PER 100 ML
pH 5.33
pH 2.93
pH 4.40

Figure X

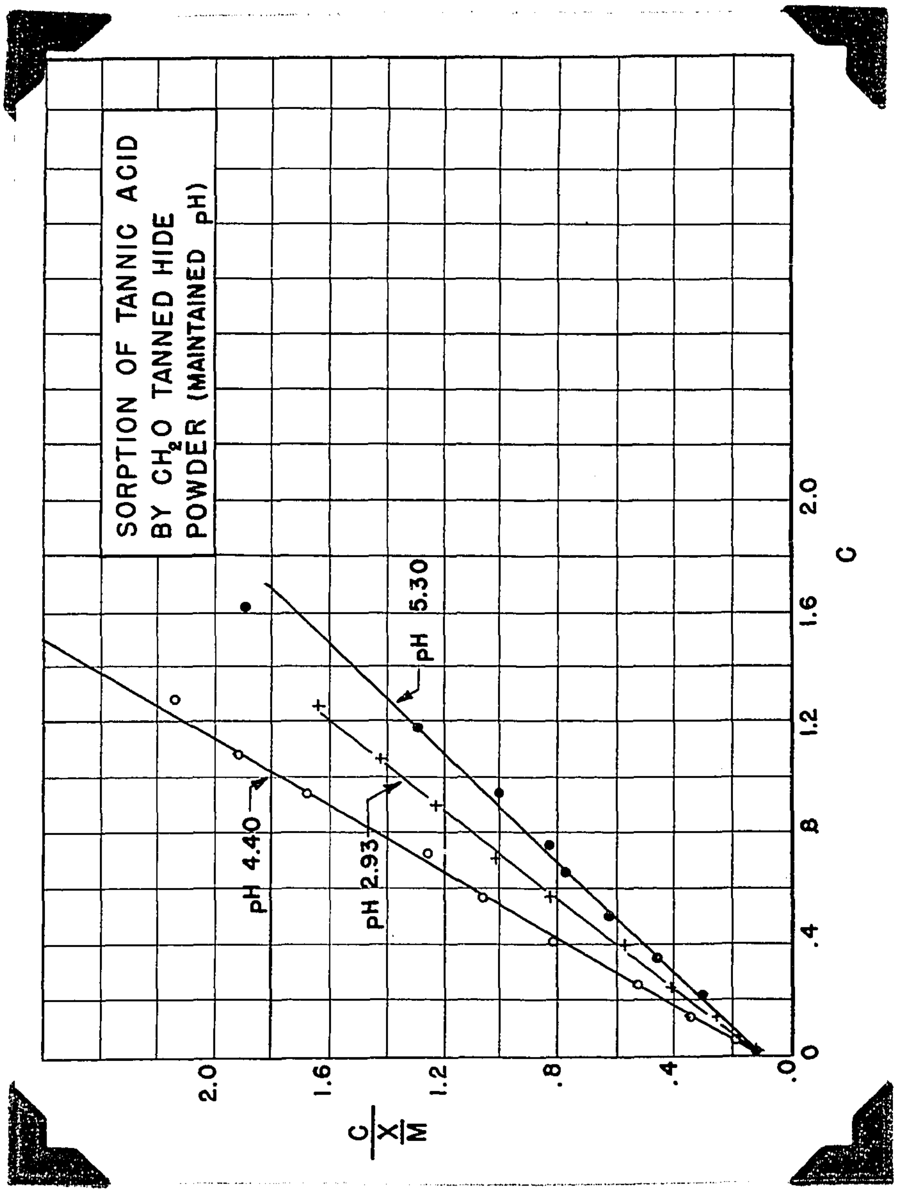

SORPTION OF TANNIC ACID
BY CH_2O TANNED HIDE
POWDER (MAINTAINED pH)
pH 4.40
pH 2.93
pH 5.30
C/(X/M)
2.0
1.6
1.2
.8
.4
0
C
.4
.8
1.2
1.6
2.0

Figure XI

TABLE XV

SORPTION OF PENTA-DIGALLOYL-β-GLUCOSE BY CH_2O TANNED HIDE POWDER MAINTAINED AT pH 5.00. Time: 24 hours.

No.	Original conc. gms. Tannin per 1 gm. Hide powder	Final conc. gms. Tannin per 1 gm. Hide powder	Equilibrium conc. gms. Tannin per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.2130	.0253	.0220	.1877	.1170
2.	.4260	.0508	.0439	.3752	.1172
3.	.6470	.0865	.0740	.5605	.1320
4.	.8510	.1400	.1275	.7100	.1795
5.	1.2760	.3440	.2988	.9320	.3210
6.	1.7010	.6350	.5510	1.0660	.5170
7.	2.1300	.9850	.8550	1.1450	.7460
8.	2.6800	1.4450	1.2560	1.2350	1.0160
9.	3.1900	1.9360	1.6830	1.2540	1.3400
10.	4.2600	2.9900	2.6000	1.2700	2.0500

B. Experimental

V. The Effect of Time on the Sorption of Tannic Acid and Tannin by Hide Powder.

Kubelka(15) studied the adsorption of fatty acids by hide powder, and claimed that equilibrium was attained within thirty minutes. Rawlins and Schmidt(16), working with the adsorption of an acid dye, Tropaeolin O, by gelatine granules, found that the amount of dye taken up by the gelatin granules increases with time, and that the maximum was reached after 120 hours. To determine what effect time has on the sorption of tannic acid by hide powder, the concentrations were the same as those previously used. The pH values were kept constant. Three sets of experiments were performed: (1) The effect of time on the sorption of tannic acid by buffered hide powder, (2) the effect of time on the sorption of tannic acid by buffered formaldehyde tanned hide powder, and (3) the effect of time on the take-up of penta-m-digalloyl-B-glucose by buffered hide powder. The time of shaking was from one to one hundred sixteen hours. The results are given in Tables XII, XIII, and XIV, and shown graphically in Figures XII, XIII, XIV, XV, and XVII.

TABLE XII

EFFECT OF TIME ON THE SORPTION OF TANNIC ACID BY HIDE POWDER

Time: 1 Hour. pH: Maintained at 5.00

No.	Original conc. gms. Tannic acid per 1 gm. Hide powder	Final conc. gms. Tannic acid per 1 gm. Hide powder	Equilibrium conc. gms. Tannic acid per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.2060	.0243	.0230	.1817	.1266
2.	.4150	.0759	.0692	.3411	.2030
3.	.6170	.1560	.1472	.4610	.3200
4.	.8280	.2700	.2570	.5580	.4610
5.	1.2390	.5410	.5100	.6980	.7310
6.	1.6570	.8670	.8150	.7900	1.0320
7.	2.0700	1.2450	1.1700	.8250	1.4180
8.	2.4800	1.6200	1.5250	.8600	1.7730
9.	3.1100	2.1000	1.9750	1.0100	1.9750
10.	4.1400	3.1100	1.9750	1.0300	2.8350

Time: 6 Hours. pH: Maintained at 5.00

1.	.2070	.0214	.0201	.1850	.1087
2.	.4110	.0606	.0574	.3504	.1655
3.	.6200	.1094	.1030	.5106	.1995
4.	.8300	.1896	.1780	.6404	.2780
5.	1.2420	.4580	.4310	.7840	.5500
6.	1.6600	.7740	.7280	.8860	.8220
7.	2.0800	1.0200	.9570	1.0600	.9030
8.	2.4990	1.4000	1.3130	1.0990	1.1930
9.	3.1150	1.9060	1.7970	1.2090	1.4780
10.	4.1500	2.8900	2.7100	1.2600	2.1500

TABLE XII(continued)

EFFECT OF TIME ON THE SORPTION OF TANNIC ACID BY HIDE POWDER

Time: 24 Hours. pH: Maintained at pH 5.00

No.	Original conc. gms. Tannic acid per 1 gm. Hide powder	Hinal conc. gms. Tannic acid per 1 gm. Hide powder	Equilibrium conc. gms. Tannic acid per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.2069	.0194	.0183	.1870	.0978
2.	.4130	.0535	.0502	.3597	.1398
3.	.6240	.0967	.0905	.5273	.1715
4.	.8310	.1640	.1536	.6670	.2302
5.	1.2420	.3200	.3855	.9220	.4170
6.	1.6520	.7240	.6820	.9280	.7350
7.	2.0800	1.0470	.9800	1.0330	.9480
8.	2.4850	1.3350	1.2530	1.1500	1.1940
9.	3.1150	1.9550	1.8330	1.1600	1.5810
10.	4.1600	2.8800	2.6699	1.2800	2.0850
	Time: 116 Hours.	pH: Maintained at pH 5.00			
1.	.2140	.0210	.0183	.1930	.0946
2.	.4140	.0534	.0502	.3606	.1396
3.	.6210	.0925	.0871	.5285	.1650
4.	.8260	.1552	.1463	.6708	.2180
5.	1.2400	.3710	.3488	.8778	.3970
6.	1.6600	.6840	.6410	.9760	.6560
7.	2.0700	1.0170	.9580	1.0530	.9100
8.	2.4750	1.3270	1.2520	1.1480	1.1000
9.	3.1300	2.1300	1.8330	1.0000	1.8330
10.	4.1500	3.0200	2.8600	1.1300	2.7500

TABLE XIII. EFFECT OF TIME ON THE SORPTION OF TANNIC ACID BY CH_2O TANNED HIDE POWDER.

Time: 1 Hour. pH: Maintained at 5.80

No.	Original conc. gms. Tannic acid per 1 gm. Hide powder	Final conc. gms. Tannic acid per 1 gm. Hide powder	Equilibrium conc. gms. Tannic acid per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.1876	.0252	.0262	.1624	.1610
2.	.3775	.0896	.0896	.2879	.3110
3.	.5625	.1860	.1860	.3765	.4950
4.	.7510	.3040	.3160	.4470	.7070
5.	.9590	.4630	.4810	.4760	1.0100
6.	1.1240	.6170	.6420	.5070	1.2670
7.	1.3070	.7640	.8000	.5430	1.4810
8.	1.5050	.9230	.9610	.5820	1.6500
9.	1.6900	1.0880	1.1550	.6020	1.8850
10.	1.8710	1.2500	1.3020	.6020	1.8850
11.	2.3400	1.6620	1.7300	.6780	2.5500

Time: 6 Hours. pH: Maintained at 5,80

1.	.1877	.0252	.0262	.1625	.1610
2.	.3784	.0695	.0722	.3089	.2340
3.	.5640	.1315	.1360	.4325	.3140
4.	.7520	.2220	.2306	.5300	.4360
5.	.9400	.3480	.3630	.5910	.6130
6.	1.1280	.5040	.5220	.6240	.8370
7.	1.3150	.6780	.7040	.6370	1.1060
8.	1.5040	.8200	.8510	.6840	1.2450
9.	1.6900	.9950	1.0320	.6950	1.4870
10.	1.8800	1.1450	1.1900	.7350	1.6200
11.	2.5500	1.5650	1.6270	.7850	2.0700

Time: 24 Hours. pH: Maintained at pH 5.80

1.	.2022	.0311	.0296	.1711	.1730
2.	.4035	.0753	.0752	.3282	.2205
3.	.6020	.1260	.1210	.4760	.2540
4.	.8050	.2040	.1955	.6010	.3250
5.	1.0100	.3132	.3000	.6968	.4300
6.	1.2100	.4570	.4375	.7530	.5810
7.	1.3940	.5800	.5625	.8140	.7670
8.	1.6100	.7760	.7540	.8340	.9040
9.	1.8200	.9200	.8850	.9000	.9820
10.	2.0220	1.0920	1.0430	.9300	1.1100
11.	2.5040	1.5960	1.5380	.9110	1.6870

TABLE XIV

EFFECT OF TIME ON THE SORPTION OF PENTA-DIGALLOYL-β-GLUCOSE BY HIDE POWDER.

Time: 1 Hour. pH: Maintained at 5.00

No.	Original conc. gms. Tannin per 1 gm. Hide powder	Final conc. gms. Tannin per 1 gm. Hide powder	Equilibrium conc. gms. Tannin per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.1880	.0158	.0176	.1722	.1021
2.	.3770	.0390	.0436	.3380	.1290
3.	.5640	.0850	.0915	.4612	.1985
4.	.7560	.1750	.5810	.5810	.3020
5.	1.1280	.4050	.4140	.7230	.5720
6.	1.4950	.7100	.7300	.7850	.9300
7.	1.8900	.9480	.9320	.9420	.9900
8.	2.3350	1.4120	1.4370	.9230	1.5400
9.	2.8150	1.8160	1.8400	.9990	1.8450
10.	3.8400	2.7000	2.7320	1.1400	2.3950

Time: 6 Hours. pH: Maintained at 5.00

No.	Original conc. gms. Tannin per 1 gm. Hide powder	Final conc. gms. Tannin per 1 gm. Hide powder	Equilibrium conc. gms. Tannin per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.1880	.0170	.0175	.1710	.0982
2.	.3790	.0381	.0385	.3409	.1123
3.	.5680	.0594	.0598	.5086	.1174
4.	.7500	.1163	.1184	.6397	.1850
5.	1.1250	.3120	.3168	.8130	.3900
6.	1.5010	.5980	.6040	1.0030	.6020
7.	1.9060	.9170	.9300	.9890	.9410
8.	2.5500	1.2830	1.3000	1.0670	1.2170
9.	2.7400	1.7970	1.8200	.9430	1.9280
10.	3.6500	2.5050	2.5400	1.1450	2.2150

TABLE XIV (continued)

Time: 24 Hours. pH: Maintained at 5.00

1.	.1883	.0127	.0129	.1756	.0734
2.	.3750	.0349	.0355	.3401	.1044
3.	.5690	.0560	.0568	.5130	.1110
4.	.7570	.0945	.0956	.6625	.1444
5.	1.1530	.2910	.2945	.8620	.3415
6.	1.5230	.5490	.5540	.9740	.5680
7.	1.8800	.7700	.7800	1.1100	.7020
8.	2.3400	1.2530	1.2730	1.0870	1.1720
9.	2.8350	1.6500	1.6670	1.1850	1.4060
10.	3.7800	2.4880	2.5500	1.2920	1.9600

Time: 116 Hours. pH: Maintained at 5.00

1.	.1877	.0146	.0148	.1751	.0855
2.	.3768	.0465	.0469	.3303	.1420
3.	.5640	.0687	.0697	.4953	.1410
4.	.7510	.1070	.1087	.6440	.1690
5.	1.1210	.2520	.2562	.8690	.2950
6.	1.4970	.5240	.5530	.9730	.5480
7.	1.8740	.7970	.8680	1.0770	.8040
8.	2.3400	1.1600	1.1800	1.1800	1.0000
9.	2.8200	1.6620	1.6820	1.1580	1.3400
10.	3.7600	2.4920	2.5500	1.2680	2.1600

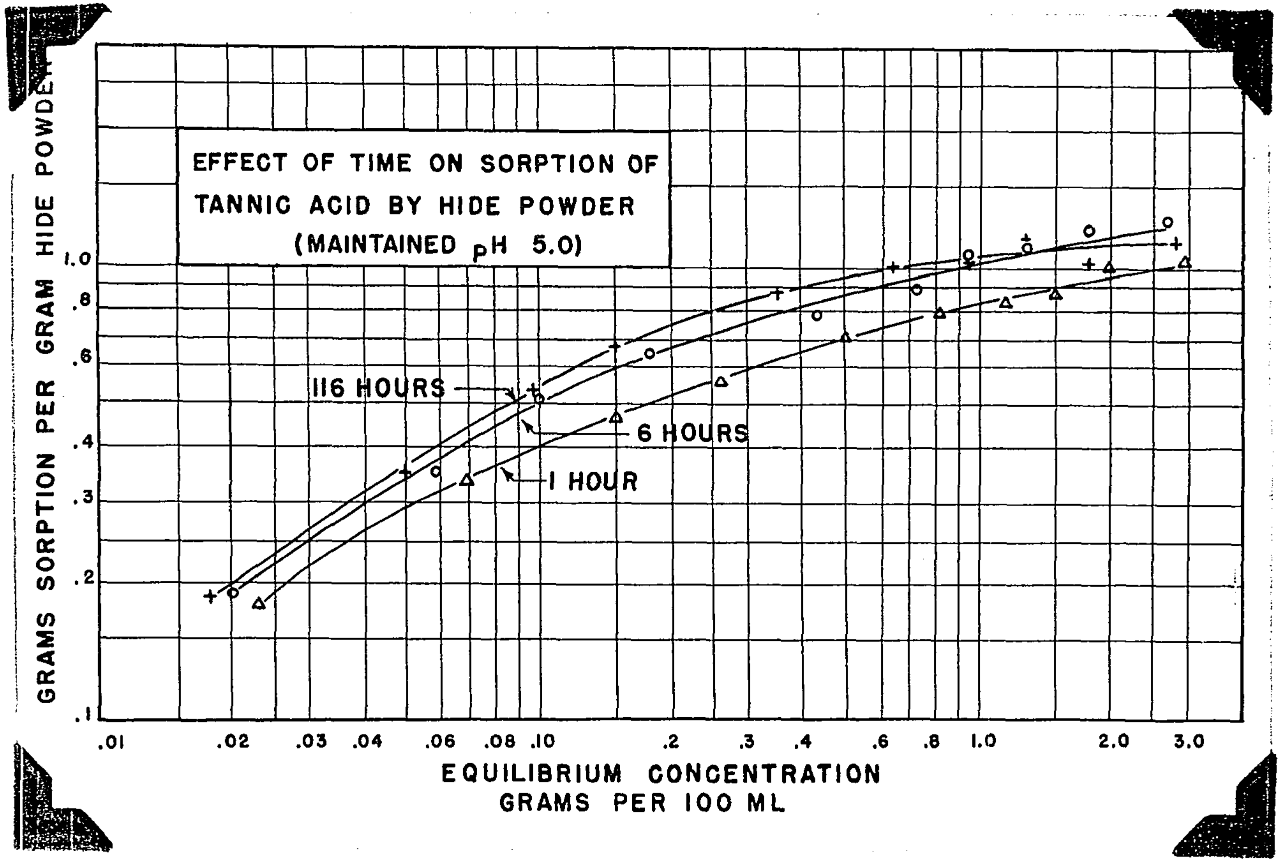
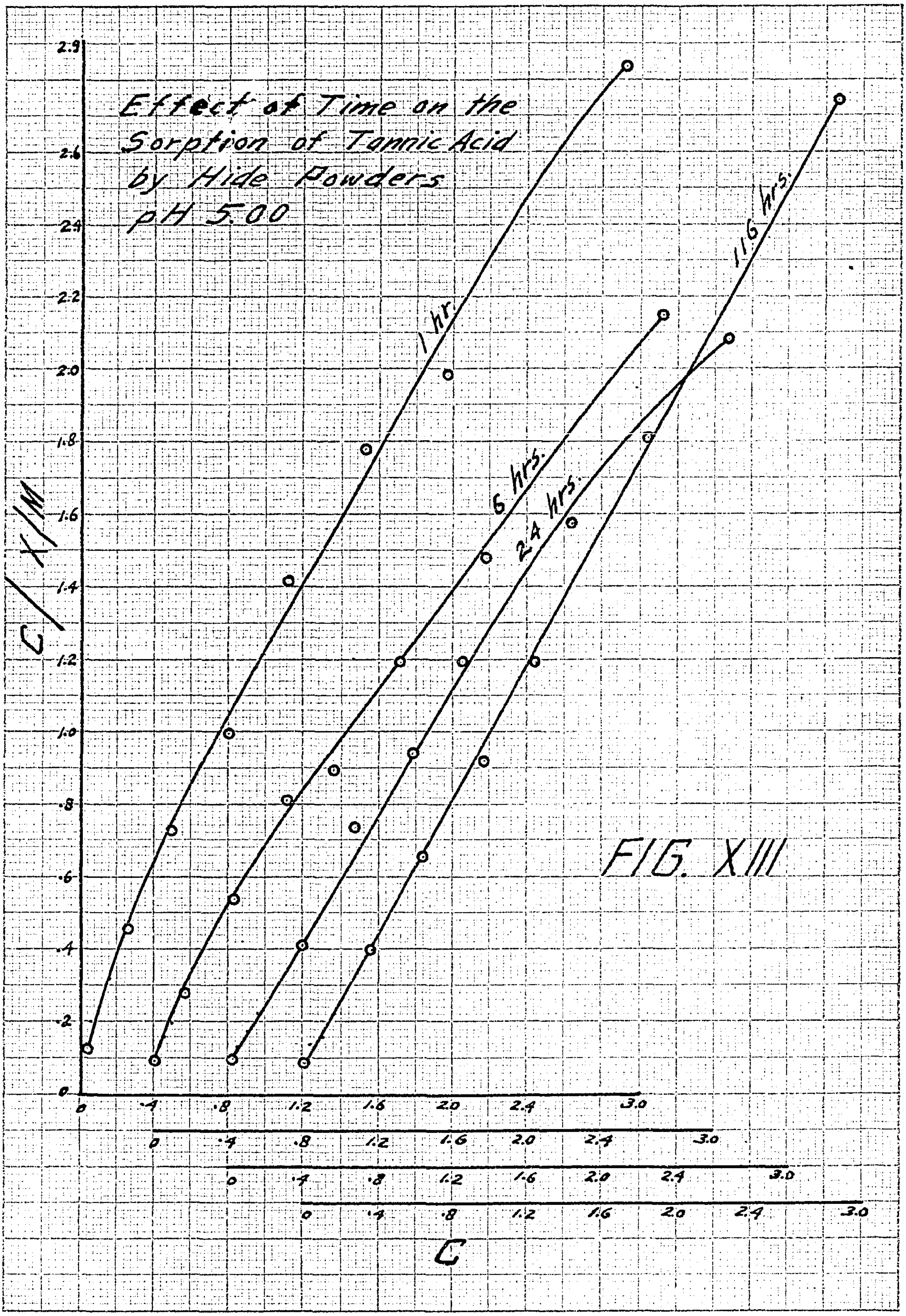

EFFECT OF TIME ON SORPTION OF TANNIC ACID BY HIDE POWDER (MAINTAINED pH 5.0)
116 HOURS
6 HOURS
1 HOUR
GRAMS SORPTION PER GRAM HIDE POWDER
1.0
.8
.6
.4
.3
.2
.1
.01
.02
.03
.04
.06
.08
.10
.2
.3
.4
.6
.8
1.0
2.0
3.0
EQUILIBRIUM CONCENTRATION GRAMS PER 100 ML

Figure XII



Effect of Time on the Sorption of Tannic Acid by Hide Powders pH 5.00

FIG. XIII

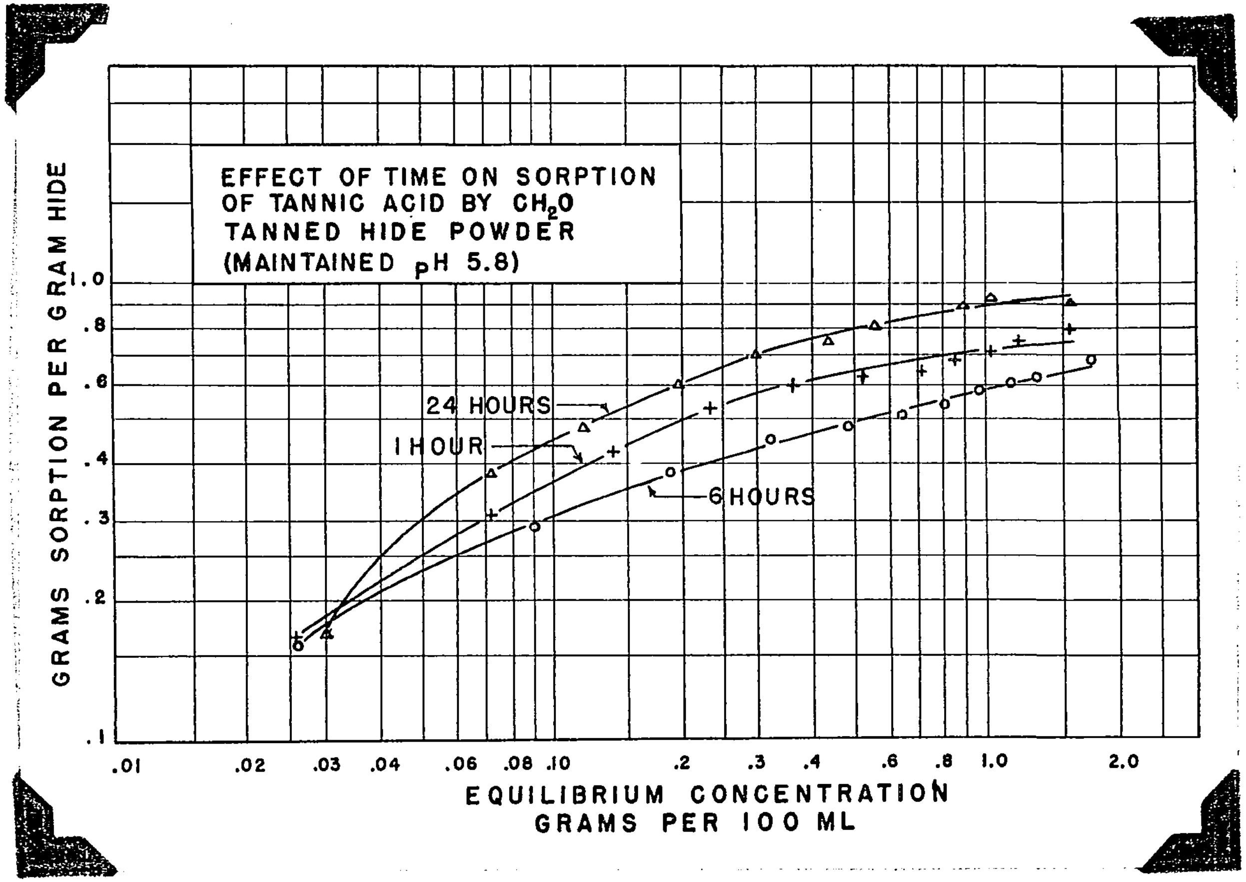
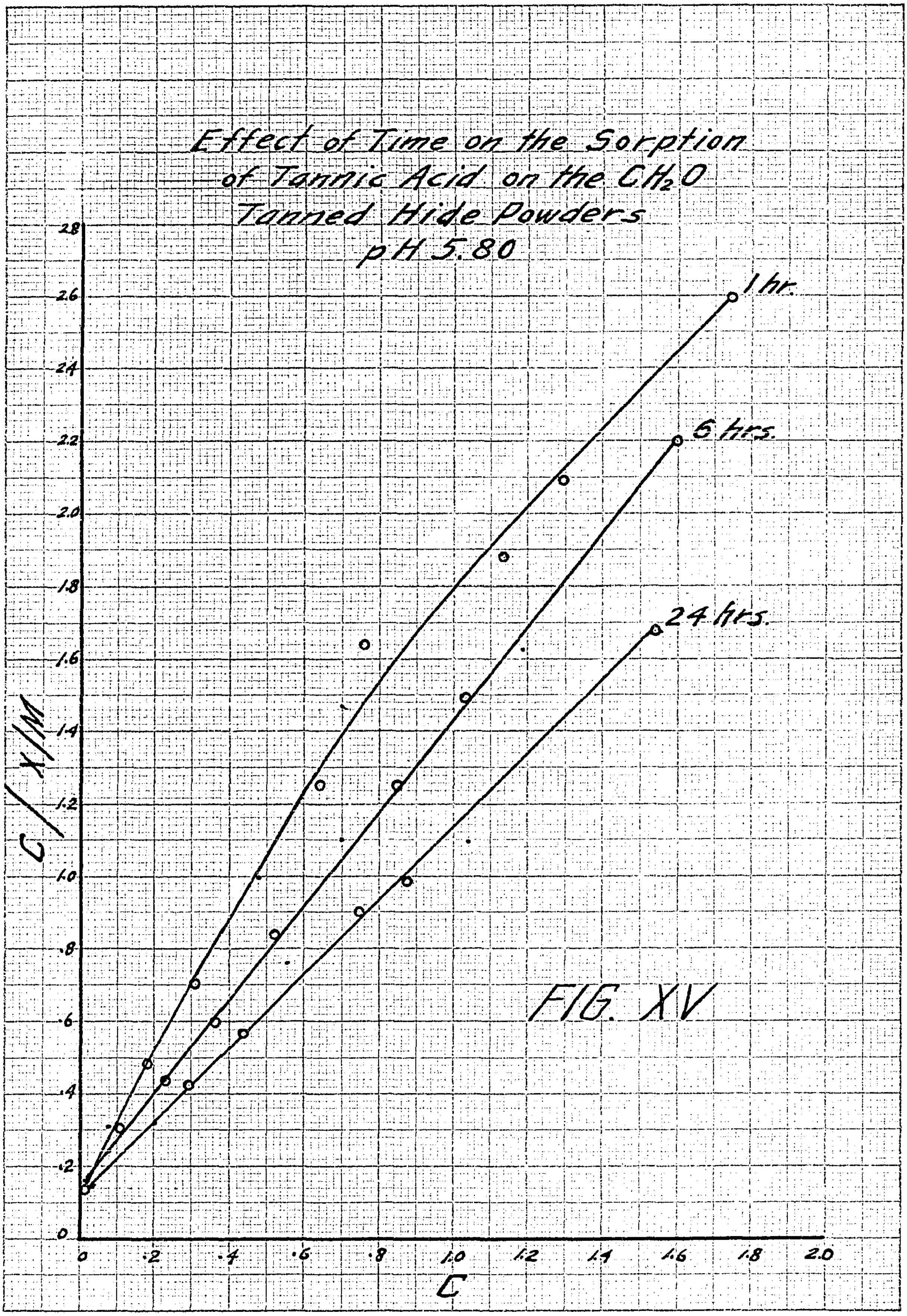

EFFECT OF TIME ON SORPTION
OF TANNIC ACID BY CH2O
TANNED HIDE POWDER
(MAINTAINED pH 5.8)
GRAMS SORPTION PER GRAM HIDE
1.0
.8
.6
.4
.3
.2
.1
.01
.02
.03
.04
.06
.08
.10
.2
.3
.4
.6
.8
1.0
2.0
EQUILIBRIUM CONCENTRATION
GRAMS PER 100 ML
24 HOURS
1 HOUR
6 HOURS

Figure XIV

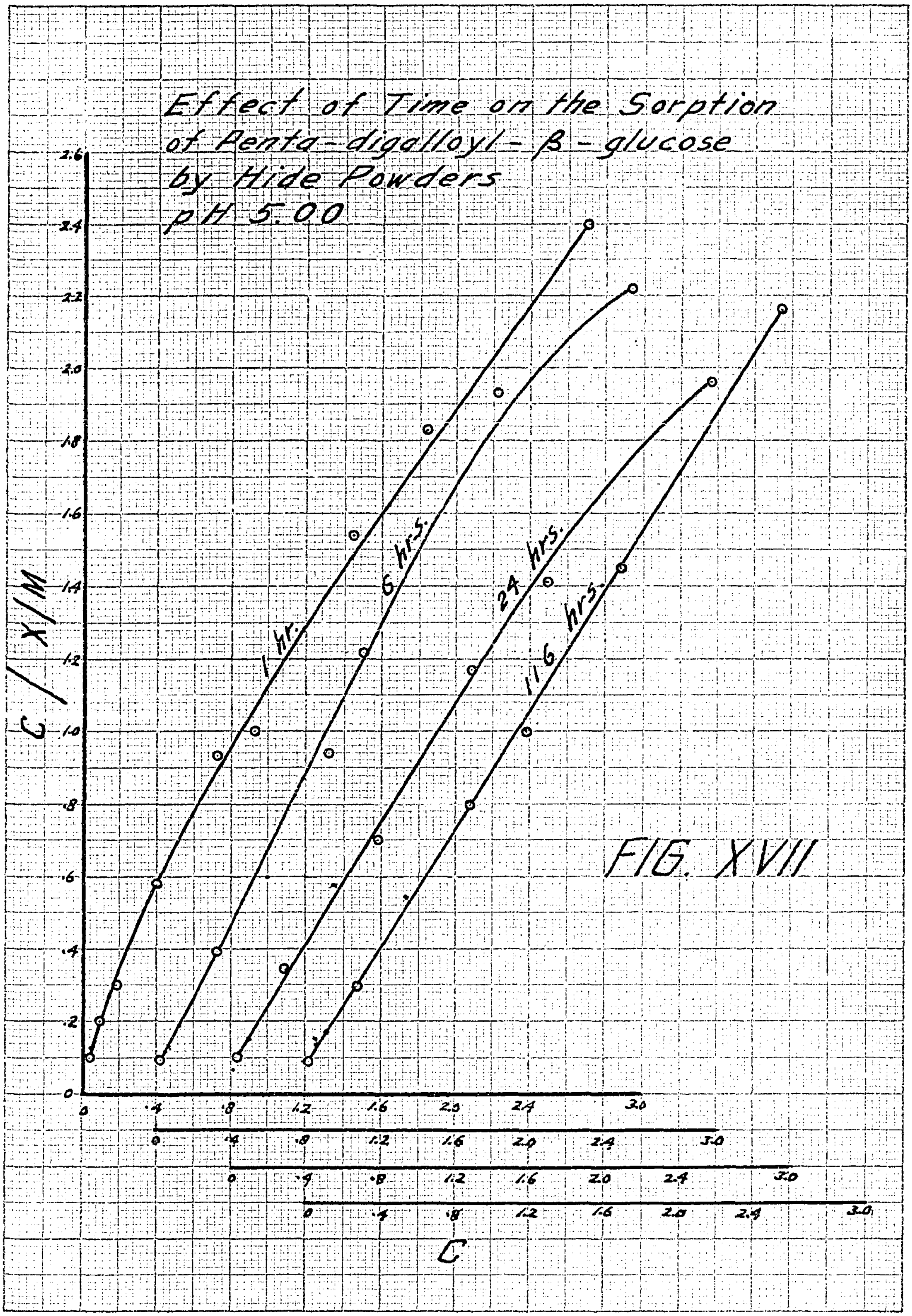


Effect of Time on the Sorption of Tannic Acid on the CH_2O Tanned Hide Powders

pH 5.80

FIG. XV

17 h



Effect of Time on the Sorption of Penta-digalloyl-β-glucose by Hide Powders
pH 5.00

FIG. XVII

B. Experimental

VI. The Sorption of Penta-m-digalloyl-B-glucose from an 85% Alcoholic Solution by Hide Powder.

When hide powder is soaked in an alcoholic solution, the number of Zwitterions is greatly reduced. Also, there is very little swelling due to the dehydration effect of the alcohol. This experiment was to determine the take-up of tannin from an alcoholic solution by hide powder. The results are given in Table XVI, and shown graphically in Figure VIII .

TABLE XVI

SORPTION OF PENTA-DIGALLOYL- -GLUCOSE BY HIDE POWDER IN 85% ALCOHOLIC SOLUTION.

No.	Original conc. gms. Tannin per 1 gm. Hide powder	Final conc. gms. Tannin per 1 gm. Hide powder	Equilibrium conc. gms. Tannin per 100 ml. solution	$\frac{X}{M}$	$\frac{C}{\frac{X}{M}}$
1.	.2112	.1160	.1086	.0952	1.1420
2.	.4260	.2833	.2640	.1427	1.8500
3.	.6370	.4660	.4340	.1710	2.5400
4.	.8260	.6340	.6074	.1920	3.1600
5.	1.2700	1.0270	.9610	.2430	3.9500
6.	1.6930	1.4350	1.3420	.2580	5.2100
7.	2.0900	1.7990	1.7060	.2910	5.8600
8.	2.6450	2.3250	2.1800	.3200	6.8200
9.	3.1720	2.8400	2.6200	.3320	7.8800
10.	4.2400	3.8200	3.5700	.4200	8.5100

C. Discussion

When the data of Table I are plotted as shown in Figure I, i.e., the grams sorption of tannic acid per gram of hide powder versus the equilibrium concentration in grams per 100 mls., a curve suggestive of an adsorption isotherm is obtained. However, when the data are plotted on a log-log scale, as given by Freundlich(17), approximately two, rather than one, straight lines are obtained, as shown in Figure II. When the effects of various pH values on the take-up of both tannic acid and tannin are taken into consideration, as shown in Figures III, IV, VI, and VIII, the results indicate that the take-up in the low concentrations is almost independent of the pH value of the system (in the range shown), but in the higher concentrations the acidity of the system plays a role. As previously stated, strict comparison cannot be made between the different series of data due to variations in the ratio of solution to hide powder, but if these variations and also the water content of the hide powder are taken into consideration, some general conclusions may be drawn. It is evident from the data and curves that in the higher concentrations, the least amount of sorption takes place when the system is around the isoelectric point of the hide powder, which Wilson shows is approximately pH 5.0. Either above or below this pH value, greater quantities of tannic acid or tannin are taken up for a given concentration. Since the free amino groups are almost completely ionized at the pH values shown, the chemical theory of tannage cannot be used to explain these phenomena in the high concentrations. According to the physical theory of tanning, the adsorption of tannin is dependent upon the surface area of the adsorbent. Since swelling of the hide powder takes place as the pH is raised or lowered from the isoelectric point, thereby resulting in greater surface area, this may account for the increased take-up. Weiser(19) states that Freundlich's equation never describes the facts accurately over any wide range of concentrations, and when high concentrations of adsorbate are used, Langmuir's(18) adsorption equation applies better than Freundlich's. When the above data are plotted according to Langmuir's method, as shown in Figures VII and IX, straight lines are obtained.

The free amino groups would be the reactive groupings if chemical combination took place between the collagen and the tannic acid or tannin. Therefore, the hide powder was tanned with formaldehyde in an alkaline solution, as previously described, to block out these amino groups. The take-up of tannic acid and tannin by this tanned hide powder is shown in Figures V, VIII, X, and XI. These graphs show that the formaldehyde tanned hide powder does not take up quite as much tannic acid as the raw hide powder, but that the take-up is still appreciable. In the case of tannin, little difference in sorption is noted between the tanned and the untanned hide powder at the same pH. The sorption of tannic acid is greater at pH 5.8 than at pH 2.93, but, again, this can be explained by the physical theory, as the swelling of formaldehyde tanned hide powder is greater at pH 5.8 than at pH 2.93. Because the amino groups are not free after formaldehyde tanning, any swelling will be due mainly to the ionized carboxyl radical, and this will be less suppressed at pH 5.8 than at pH 2.93; consequently, greater swelling will take place at the higher pH. The sorption of tannic acid by formaldehyde tanned hide powder appears to be independent of the pH of the system when low concentrations are used. Again, when the data are plotted according to Langmuir's adsorption equation, straight lines are obtained.

In Figure VIII is shown the sorption of tannin by hide powder from an 85% alcoholic solution. The sorption in this case is less than from an aqueous solution, and the "saturation" point of the hide powder is not approached; consequently, either Freundlich's or Langmuir's equation will give a straight line. The sorption is not great for two reasons: (1) the hide powder in an alcoholic solution has little or no swell, and, therefore, the surface area is at a minimum, and (2) when the adsorbate has a great attraction for the solvent, only a small amount will be adsorbed by the adsorbent, and tannin has a greater affinity for alcohol than it does for water.

In many of the examples cited above, the point of highest concentration, when plotted according to Langmuir's equation, does not fall on the straight line. It was thought that perhaps at these high concentrations insufficient time of contact did not allow the sorption to go to completion. To determine the effect of time on the sorption of tannic acid and penta-m-digalloyl-B-glucose by buffered hide powder and buffered formaldehyde tanned hide powder, data were obtained and plotted as shown in Figures XII, XIII, XIV, XV, and XVII. From these curves, it can be seen that when sufficient time of contact is allowed, the sorption data follows a straight line when plotted according to Langmuir's adsorption equation.

D. Summary

(1) The sorption of tannic acid and penta-m-digalloyl-B-glucose by both buffered hide powder and buffered formaldehyde tanned hide powder was determined under various controlled conditions.

(2) By the methods used, the sorption of tannic acid and tannin from dilute solutions appears to be nearly independent of the pH value of the system. When stronger solutions are employed, the amount of sorption depends in part upon the pH of the system.

(3) The sorption of tannic acid and tannin at any given concentration is minimum when the system is at the same acidity as the isoelectric point of the hide powder, and increases when the pH is either lowered or raised from the isoelectric point.

(4) Buffered formaldehyde tanned hide powder does not take up quite as much tannic acid from solution at a given concentration and pH as does buffered hide powder. No such difference was noted when tannin was the adsorbate.

(5) The sorption of tannin from an 85 per cent alcoholic solution by hide powder was small and followed Freundlich's isotherm.

(6) Because the range of concentrations used was great, Freundlich's method of log-log plotting of the data does not result in a straight line.

(7) When the data obtained ~~is~~ are plotted according to Langmuir's method, which is applicable over a great range of concentrations, straight lines were obtained if sufficient time were allowed for completion of the sorption.

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