THESIS
ON
TANNIC ACID
FOR
DEGREE & B.S.
IN
SCHOOL & CHEMISTRY.
BY
Ernst Speidel.
In this paper on tannin acid
or tannin, I will try to give a discussion as to its proper
basis and composition and also give a statement of my
investigations, as to the relative values of the different
methods of its estimation.

Tannin though a well known
substance, very frequently found in nature, very much
used in the arts either directly or indirectly, is a compara-
tively strange substance to the chemist, and that he is
unacquainted with it, but its occurrence and its com-
bination with other materials, and the difficulty in ob-
taining it in a pure state has baffled the attempts of men
who have endeavored to throw a light upon this subject.
The literature of tannin is
rather scarce and there are but few who have undertaken
to publish and put their work before the world. None of the
writers on this subject seem to be satisfied with their results.
There is always something that does not turn out according to the satisfaction of the investigator.

Tannin is found distributed in various plants, either in the bark, leaves, or fruit, or indeed as it may happen throughout the whole plant. Tannin is found in considerable quantity in gall nuts, which form the principal source from which the tannin acid of commerce is taken. It is also found in the tasts of the oak, of similar and in the leaves of the eucalyptus. From these latter sources tanners secure their tanning material. Aqueous extracts are made of the barks or leaves as the case may be, and these are used directly, or are boiled down to a syrupy extract, for preservation and convenient transportation.

Pure tannin is obtained in the following manner: A small quantity of powdered gall nuts is treated with aqueous ether. This extract contains all the tannin and gall acid, and after the ether is driven off the tannin and gall acid remains as an amorphous yellow mass. I obtained mine and from this emanate, but
from the Luminic acid of The long store. This is the same as the

substance obtained in the preceding process only some of the
gallic acid had been taken out according to the following

method.

First Solution

2 oz of commercial tannic

diluted acid is placed in a well-stoppered bottle with

a mixture of 9 parts of ether and 2 parts of

water; with frequent agitation. This mixture is allowed to

remain in contact twenty hours. Then the whole is transferred

to a separating funnel and after standing some time, three

layers will be formed. The uppermost is pure ether which

holds in solution all the gallic acid; the next layer is

aqueous ether containing both gallic and tannic acid; the

third or last layer contains the tannic in a pure state.

This bottom layer is drawn off into an evaporating dish

after which it is placed on the water bath and brought to

boilness, precautions being taken to exclude all light. Be-

causethis has an unfürious effect upon tannin at this

state of its production; it is very easily converted into gallic acid
When exposed to light, tannin acid always holds a consider-
able quantity of hydroscopic water, its affinity for which is
so great that heat can not drive it off without destroying
the tannin itself, and in order to make it perfectly dry,
it is placed in a sulphuric acid and allowed to stand in
some dark place. The product thus obtained is pure tannin,
it is monogalactose, very soluble in water and in alcohol,
but is insoluble in pure ether.

With regard to its formula,
the different chemists do not agree. Roseve in his Elements
of Chemistry (Page 337) gives it this formula C_{27} H_{22} O_{7}, Stuecker
in his organic chemistry (Page 634) states it as C_{14} H_{10} O_{9},
Mulder (Zeitschrift der Chemie Vol 11 Page 316) has
C_{28} H_{10} O_{8} for this formula, and in the same volume and page
Soove has C_{24} H_{10} O_{8}

To determine the question if possible,
I made a series of combustions with tannin of my own
preparation. In this work I ignited the tannin in the
presence of copper oxide. In the first two experiments I did not take precautions to exclude moisture and carbonic acid from the air I drew through the contraction tube. In the last two experiments the air first passed through two U tubes, the first containing a strong solution of potassium hydroxide and the second calcium chloride. The following results I obtained.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tannic acid</td>
<td>3.320 g</td>
<td>6.111 g</td>
<td>0.679 g</td>
<td>0.691 g</td>
</tr>
<tr>
<td>Carbon</td>
<td>40.903%</td>
<td>62.22%</td>
<td>56.62%</td>
<td>56.89%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.039%</td>
<td>2.98%</td>
<td>4.19%</td>
<td>4.13%</td>
</tr>
</tbody>
</table>

Lowe (Fresenius Zeitschrift der Chemie Vol 29 Page 213) in his research finds Carbon 55.42% up to 62.19% and Hydrogen from 4.69% down to 4.06%.

Owing to the partial ignorance of this substance, its estimation, as found in nature, has been the stumbling block of the chemists for the last thirty years. Methods of separation and of estimation have been devised and used by very able men. The results obtained in some cases
were very flattering but never yet have they been proven to be true.

Tannin and the process of its estimation will remain in obscurity until it can be perfectly isolated so that it can be placed by its own definite characteristics into its proper place. That is after different investigators have agreed upon the mode of investigation, then and not until then, will the results of determinations of tannin be reliable.

Tannin, as some writers claim, belongs to the group of glucosides, being readily converted into glucose and gallic acid when exposed to the air or when it is treated with dilute acids. If forms an insoluble compound with gelatine. With ferrie compounds it forms green or black precipitates.

(Strecker, Organic Chem. Page 726) while Shulder and others claim that it is an anhydride of gallic acid. But there will be a diversity among chemists on this subject, until
Tannin is found to be a definite compound, what ever be the source from which it is derived. That is to say, at the present time there seems to be a great variation in the tannins of the different plants. Tannin from oak bark being unlike that of sumac, while that of sumac again is different from the King tannin; in fact there is very little identity except in the power to precipitate gelatine.

In my investigation I find that tannic acid is not a glucoside; that there is a reaction when a tannic acid solution is added to some Fehling's liquor. I admit, and on boiling there is a separation of a red substance resembling in color the reduced copper, but on inspection I found it not to be such, it is a material known as oak red. I washed some of this red substance, and tested for copper but it would not give any reaction.

In my work I first took a solution of pure tannic acid and boiling it in the presence of Fehling's solution, I obtained a heavy deposit of reduced copper, so it seemed to me. After this I took a second quantity.
of the tannin solution and precipitated the tannin with ammonium zinc acetate. After filtering and thoroughly washing it with hot water, I dissolved it in dilute sulphuric acid. Having well washed the paper on which the filtrate had been deposited, I then placed filtrate and washings upon the sand bath and treated for one hour, added five parts of water and finally after neutralizing with sodium hydroxide I tested with Fehling's solution but no reaction took place. I tried this experiment with solutions of pure tannin four times but failed each time, not only in these but also in experiments with hemlock extract, and an extract made from black oak bark.

In consequence of all these failures to reduce copper I am led to conclude that it is not a glucoside and that the method proposed by some chemists for estimations of tannin by converting it into glucose by boiling with dilute acids and titrating with Fehling's solution and then computing it from glucose found is false and erroneous, because this titration
is based upon the fact that grape sugar or glucose reduces copper, and as there is no reduction of copper with tannin treated according to this method, it is not applicable.

Among those who have devoted considerable time and study to this subject, and who have devised methods for the estimation of tannins, Proust that is first and foremost. His method is probably the oldest, and those methods most of others which use chamaeleon for an oxidizer are merely modifications of this. Others who have proposed methods are Meister and Barbi and Jean.

The first method which I used was that of Boven that (Forschungs Gletschrit Vol. 22, Page 676). The titrate the solution of tannin after the addition of a standard indigo solution, with a standard solution of potassium permanganate whose action on iron and oxalic acid is known. Then in a second portion the precipitate is precipitated. The tannin with a solution of gelatine in saturated salt water common (table salt) removes the gelatine tannate by.
filiation, and finally after addition of the indigo solution to the filtrate he titrates the so-called non-tannates with potassium permanganate. The quantity of potassium permanganate consumed in the oxidation, after the indigo is first deducted in each case, and the difference between the remainders represents the quantity reduced by the tannin present.

The results in this method vary with the strength of the solution, and the computed value does not agree with the real values. This can be avoided by estimating the amount of potassium permanganate which is used in titrating the gelatine. This method, though the oldest in practical use is subject to several objections. First, the amount of time required in the estimation, second, the unreliability of the results obtained, and third, solutions containing gelatine and gelatinous precipitates, as in this method, are always very difficult to filter and cause loss of a great deal of time. Again there are so many different standards to test before active work can
be begun. The chemaceton must be standardized with respect to the indigo, to tannin and to gelatine. I find that a solution containing undissolved gelatine is liable to form a froth on top, which while titrating will hold some of the indigo and will not give it up unless it is boiled. Besides holding some of the indigo, the final reaction is hard to determine, for when the indigo is all devitalized, the solution will return a greenish tint owing to the particles of blue floating through the yellow solution. This difficulty does not take place unless the solution has stood some time. The solutions and their respective strengths I will give under the head of Rentaceros method.

Rentaceros method of estimation:

Tannin, \( \text{Zeitschrift der Chemie Vol 7, p 405} \) is a modification of Loewenthal's. In stead of precipitating with gelatine he filters through animal char coal to remove the tannin.

Rentaceros method as he describes it depends upon the power of char coal to remove
Tannin from solution

The objection often brought forward

That other ingredients of oak bark are oxidized by potassium

permanganate, is met by Heubner in this way, he titrate

the whole with potassium permanganate and determines the

whole of oxidizable matter. Then adds animal charcoal to the

dilution. This takes out the tannin, this is filtered and

titrated again. The difference of the two titrations being the

tannin. The solutions in this method (and I need the

same in the preceding) are prepared in the following manner.

Indigo Carmine Solution.

30 gr. of pure plastic indigo Carmine are dissolved by shaking
in one litre of cold water. It is then filtered and put

into well-stoppered bottles of about 250 cc capacity, after this

the bottles are warmed at 70° for one hour then stoppered

and put away ready for use. (The solution I had was

30 gr. in 2 litres of water.) The blue color of this solution

must when 20 c.c. are diluted to 750 c.c. with the addition
of 10 c.c. sulphuric acid, and treated with a potassium permangan-


ganate solution, turn from a greenish yellow to a clear golden yellow. If this is not the case and reddish or brownish tannin solutions appear the indigo must not be used.

**Tannin Solution**

2 gr Tannin dried at 100° are diluted in one litre of water. The best proof of the purity of tannin is the following. A small quantity of the solution is treated with a dilute solution of potassium cyanide; if it turns red or violet some gallic acid is present. This solution easily gives an opportunity for the formation of fungus. It is kept in small well stoppered bottles of 15 cc capacity after it has been warmed for some time at 70°.

**Potassium Permanganate Solution**

10 gr to 6 litres (I used 1 gr to the litre)

The potassium permanganate is standardized, first by diluting 20 cc of the indigo solution to 750 cc after adding 10 cc dilute sulphuric acid and then vibrating with the potassium permanganate solution. The same operation is performed after 10 cc of tannin solution.
have been added.

The only objection I have, and can
find against this method, is that the animal char-
coal also absorbs the coloring matter with the tannin, thus giving
me a somewhat greater result.

I prepared the animal charcoal
by boiling it in concentrated hydrochloric acid and then wash-
ing until no trace of chlorine was found when the wash water
was tested with silver nitrate.

I first standardized my indigo
solution mixed with 8 cc of dilute sulphuric acid. I placed
10 cc of indigo in a large beaker, then titrated it with chamo-
corn solution. For the different solutions I had these results:

<table>
<thead>
<tr>
<th>Indigo Sol.</th>
<th>Sulphuric Acid</th>
<th>C C Potassium Per Manganese</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 cc</td>
<td>8 cc</td>
</tr>
<tr>
<td>2</td>
<td>10 cc</td>
<td>6 cc</td>
</tr>
<tr>
<td>3</td>
<td>10 cc</td>
<td>6 cc</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

I next standardized my potassium permanganate with
reference to tannin solution. The following are the results secured.
with tannin solution containing 0.6 gr to the litre. 10 cc of Indigo 6 cc H.S.O₄ 5 cc tannin required

\[
\begin{align*}
&39.4 \\
&38.7 \\
&39.5 \\
&40.0 \\
&40.1 \\
&38.6 \\
&38.5 \\
&39.8
\end{align*}
\]

Cubic centimeters

Potassium permanganate

Average 39.4

Now subtracting from this 17.5 cc for the indigo I have 21.9 cc potassium permanganate which is equal to 0.025 gr of tannin

The first sample of tanning material I had was extract of hemlock, of which I took 0.6 gr and diluted it to one liter. Of this solution I used 6 cc for each titration.

5 cc Extract 10 cc Indigo 6 cc sulphuric acid (equally)

\[
\begin{align*}
&20.4 \\
&20.6 \\
&20.5 \\
&20.2 \\
&20.6
\end{align*}
\]

Cubic centimeters

Potassium permanganate
Average 20.46 cc of $\text{H}_2\text{Mn}_2\text{O}_7$. Then in accordance with the directions of Bunsen I took 5 cc solution and precipitated the tannin with gelatine. After filtering and adding 10 cc of indigo and 5 cc sulphuric acid there were required for the titration

19.4
20.2
19.4
19.8

Cubic centimeters

Potassium permanganate

Average 19.70 cc.

20.46 cc - 19.7 = .76 cc $\text{H}_2\text{Mn}_2\text{O}_7$ required to oxidize the tannin. Now if 22 cc $\text{H}_2\text{Mn}_2\text{O}_7$ to oxidize 0.25 gr tannin .76 cc will oxidize .0008636 gr or 3.45 % of tannin. Since the quantity used in the solution was so small I found it was too weak to be reliable. I then dissolved 22.6911 gr of extract in one litre of water and with this solution I obtained the following results.

Indigo 10 cc
Sulphuric Acid 5 cc } equal 19.2 Cubic cent.

19.2 Potassium permanganate
Tannic acid 5 cc  41.2  Cubic centimeters
Indigo 10 cc  equal  41.3
Sulphuric acid 5 cc  41.2  Potassium permanganate

Hemlock extract 5 cc  36.4  Cubic centimeters
Indigo 10 cc  equal  36.6
Sulphuric acid 5 cc  36.4  Potassium permanganate

Average 36.5

Hemlock extract without the tannin its being taken out with

Gelatine 5 cc  22.8  Cubic centimeters
Indigo 10 cc  equal  22.9
Sulphuric acid 5 cc  21.6  Potassium permanganate

Average 22.18

36.5 - 22.18 = 14.32 H₂O₂ 10 m. C₂H₂O₂H required to oxidize the tannin
If 22 cc oxidize 0.25 gr tannin, 14.32 cc will oxidize
0.167 gr tannin and having 11.34 gr extract in 5 cc add,
the percentage of tannin will be 14.338 %
With Neubauer's method I obtained the results given below. With a solution of 5 gr. extract in one litre, the results obtained were very unsatisfactory, but with the solution containing 22.6911 gr. in a litre they were much better.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Volume</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemlock extract</td>
<td>5 cc</td>
<td>36.4 cc</td>
</tr>
<tr>
<td>Indigo</td>
<td>10 cc</td>
<td>36.6 cc</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>5 cc</td>
<td>36.4 cc</td>
</tr>
</tbody>
</table>

Average 36.5

Solution filtered through charcoal

<table>
<thead>
<tr>
<th>Substance</th>
<th>Volume</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indigo</td>
<td>10 cc</td>
<td>20.5 cc</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>6 cc</td>
<td>21.6 cc</td>
</tr>
</tbody>
</table>

Average 20.7

36.5 - 20.7 = 15.8 cc. The amount of \( K_2 MnO_4 \) used by the haemin. Then we have 22 cc \( K_2 MnO_4 \) = 0.025 gr. haemin

\[ 15.8 \text{ cc } K_2 MnO_4 \times 0.019954 \text{ gr. haemin } = 0.03176 \text{ gr. haemin} \]

Jean's Method
found that tannin and gallic acid combine directly with iodine in the presence of sodium carbonate, and that the quantity taken up is directly proportional to the amount of tannin or gallic acid present. Upon this fact Jean has based a method for volumetric estimation of tannin. Since the solution is of a red color we cannot add the starch paste directly to the solution, but in order to determine the end of reaction we must test by means of starch paste on paper. Other extracts of the bark should have no disturbing effect upon the process. If the solution also contains gallic acid two titrations are necessary. The one must be direct, and the second one after the tannin has been removed by gelatin.

This method requires a great deal of time and very careful titrating. I prepared a solution of iodine by dissolving 8 g of iodine with enough potassium iodide to make it all dissolve in one litre of water.

The sodium carbonate used solution containing about 10% Na₂CO₃. I found that by using 10 c.c. of Na₂CO₃ solution the results obtained are always
constant. The vibrations I made were very numerous but the results obtained varied greatly until I had prepared a second fresh solution of iodine when the results were very satisfactory. The following is a record of a series of readings:

<table>
<thead>
<tr>
<th>Tannin</th>
<th>Na₂CO₃</th>
<th>Iodine</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 c.c.</td>
<td>10 c.c.</td>
<td>31.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.2</td>
</tr>
</tbody>
</table>

Average 31.4

Hence 31.4 c.c. iodine solution are equivalent to 0.05 grams tannin. With a solution of 22.6911 g extract in a thousand cubic centimeters of water I obtained the following results:

Extract solution 6 c.c. \{ + Na₂CO₃ 10 c.c. \} equal

\{ 11.5 \}
\{ 11.7 \}
\{ 11.8 \}
\{ 11.4 \}
\{ 11.5 \}
\{ 11.6 \}

Average 11.58

Vibration after the tannin had been removed by precipitation
Solution less tannin 5 cc
\( \text{Cu}_2 \text{CO}_3 \) 10 cc
\( \text{equal} \)
\( 2.2 \) Cubic centimeters
\( 2.3 \) Iodine

Average 2.14

11.58 - 2.14 = 9.36 cc of iodine used by the tannin, then
if 31.4 iodine satisfies .05 gr tannin 9.36 cc will satisfy .048
gramms, and in this solution give us this percentage of

\[ \text{tannin} \times \frac{11.34 \text{ gr extract}}{0.014904 \text{ gr tannin}} = 100 \times 2 = \]

13.17% of tannin.

**Barburi's Method.**

[Presseins zeitschrift der deutschen Chemie Vol 16 p123] This con-
ists in precipitating the tannin with ammonical gine
acetate, washing the precipitate with hot water, dis-
solving the latter in dilute sulphuric acid, diluting
the solution with potassium permanganate. After
Barburi had failed several times in obtaining good
results with other methods, he tried this process.

The tannin is precipitated with ammonical gine
acetate. The solution with the precipitate is forced until
one third of its volume is evaporated. After it has cooled it is
filtered, the precipitate washed with hot water and then dissolved
in dilute sulphuric acid. The solution is then filtered from those in-
soluble substances that may be present and the filtrate treated with
chamalot solution. This method always produced uniform results.
It is very profitably applied in
this direction as it gives constant results and also excludes all color-
ing matters and foreign substances from the solution to be titrated.
I find that in the washing the precipitate it is better to wash
first with cold, and then with hot water for, if first washed
with hot water it gives rise to a formation which is relative like
in action and appearance. This is of considerable hindrance in
filtering and washing when the precipitate is on the filter.

Table 27.6911 gr diluted to 1000 cc

<table>
<thead>
<tr>
<th>10 cc Solution</th>
<th>36.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 cc Indigo</td>
<td>32.2</td>
</tr>
<tr>
<td>Equal</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.7</td>
</tr>
<tr>
<td></td>
<td>33.6</td>
</tr>
<tr>
<td>Average</td>
<td>34.1</td>
</tr>
</tbody>
</table>

34.1 - 19.2 = 14.9 cc K₂Mn₂O₇ used in oxidizing the tannin. How
of 22 cc K₂Mn₂O₇ oxidized 0.25 gr of tannin 14.9 cc oxidized 01683
tannin, having used 23.69 gr extract, I get 7.46% tannin.

In all of these methods, I found that the solutions of the tanning materials must be rather strong. I first had a solution of hemlock bark 5 gr extract in a litre of water, with all four of the methods I used, I could not obtain any satisfactory result. A solution having from 18-25 gr. extract in one litre of water is about the best.

In order to test the accuracy of the results in the preceding estimations. I treated 30.7269 gr. with a mixture of ten parts of ether and three parts alcohol for some time, decanting as the residue settled. I then brought the whole including the washing down to dryness, after weighing, I had 4.2836 gr. of tannin and coloring matter. Computing I find it to be 13.94% tannin.

Now comparing the results of the four methods of estimation, we have the following: Löwen that 14.338%; Jean 13.11%; Barthi 7.46%; Kneuhauser 7.91%. We find therefore that the results obtained by methods of Löwen that and Jean are the most accurate and reliable. By Jean's method the
cotton has no reaction upon other extracts of the bark, in both methods the coloring matter or gallic acid plays a part in the titration and takes up some of the $H_2$ $H_2$ $O_7$ or iodine as the case may be. Now since the materials acted upon by the titrating liquids are the most essential ingredients in tanning solutions as used by the tanner, the results obtained by Loomes and that and Jean's method give the tanner an exact statement as to the value of the tannin or solutions there from.

In the methods of Barbieri and Bentham the coloring matter is taken out and does not enter into the calculation, therefore for a true statement with reference to tannin alone there are the best methods.

And again of these methods I found Jean's the most practical, because of the first two it requires neither as many titrations nor as many solutions as Loomes and that, and of the last two, I must say both are very good and reliable. Barbieri's method was the best as it required but on titration though it took more time in preparing for the titration.