THESIS

on

A Chemical Study of Western Oregon Nutgalls.

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A CHEMICAL STUDY OF WESTERN OREGON NUTGALLS.

Few discoveries of any importance have been the result of a moments happy coincidence; rather have they been the fruit of many hours of tedious thought and experiment. This is especially true in the realm of organic chemistry. Here, where progress is made only by the most painstaking experimentation, extensive fields lie unexplored by the chemist and the advance made during each decade over the achievements of the preceeding one but opens new avenues for endeavor and research.

The history of the identification of tannin, or tannic acid as a proximate principle is no exception to the general rule, and is the result of about half a century of experimentation by a score of chemists and apothecaries. Previous to 1790, the only sources of information concerning anything related to tannin were to be found in the history of nutgalls, tan bark, and the leather industry. The reactions occurring in the tanning of leather were not even suspected at that time to be chemical in nature, and writers of a later date speak of astringent action of, galls as being due to an unknown and unnamed principle.

Dr. Wm. Lewis, of London, spoke of a principle, occurring in infusions of various crude drugs and especially of nutgalls, which formed a dark liquid, very useful

in dyeing, when added to a solution of green vitriol, and many English writers ascribe to him the credit for part of the discovery of tannin.

In 1786, a number of extensive experiments with galls were performed by Scheele, resulting in the identification of gallic acid, and, in 1791, Dize' repeated these experments and described a substance obtained by an extraction with ether as a dark resinous principle. The publication of these experiments led to extensive research work in this line by DeYeax, a French chemist, and, in 1793, he published the results of elaborate experiments on Aleppo galls. Other writers and experimenters along this line appeared at about this time, but the men to whom special credit is due for the discovery and identification of fannic acid are Dijon, Scheele, Berthelot, and Fourcroy while to Hugo Schiff and Julius Lowe must be given the credit of independently establishing our knowledge of this plant principle.

Nutgalls, or galls, the principal source of tannic or di-gallic acid so far as pharmacy is concerned, are pathogenic growths occurring on the branches of Quercus lusitanica or other spedies of oak and caused by the puncture and deposited ova of the insect Cynips Gallae ~~tinctoria~~ tinctoria or other insect of like habits. They are hard heavy subglobular grayish balls from the size of a pea to the size of a cherry. Structurally they are composed of a hard outer shell with a more or less pithy portion surrounding a center of stone cells. In

this hard center portion are the eggs and larvae of the insect. Upon becoming a fly, each soon gnaws its way to liberty, leaving a small round hole as evidence of its pormer presence.

The pharmaceutical value of the galls depends a great deal upon the habitat and the host. The best are found in Asia Minor and along the Mediterranean Basin, where they are known to have contained as high as seventy per cent of astringent principle. Besides these there are the German galls, the Japanese or Chinese galls, and the American galls. These latter were not analyzed until of late years, and, although possessing about the same medicinal value as the English varieties, are not nearly so well known.

The nutgalls occurring on the oak trees west of the Rocky Mountains have apparently received no attention from pharmacists and chemists in general. They are of two general varieties. A small, hard, globular gall of a dark gray color is found in great abundance on the grub oaks of the Willamette Valley. They seldom grow larger than a good sized pea and are often half eaten away by the developing insect.

The other variety commonly seen is very large and is conspicuous on account of its white color. It is pithy in internal texture, with a hard center of stone cells. During the growth of the gall it contains a large quantity of very astringent liquid and often at-

tains the size of a person's two fists.

Besides these there are three other varieties of galls, but they are seldom found in any quantity and seem to yeild a much smaller per cent of di-gallic acid.

During the last fifty years many methods of analysis have been proposed by different chemists, but each has its objections. Among those first used was the precipitation of the tannin from a solution as tannate by the use of Copper or lead acetate. This soon fell into disuse, the principal objection to it being that it precipitated the small percent of gallic acid present in a solution made from the galls as an insoluable gallate, thus preventing its determination and rendering the quantitative analysis of di-gallic acid incorrect.

The method used perhaps to the greatest extent at the present time depends upon the oxidizing action of potassium permanganate upon tannic acid. The practicability and delicacy of this reaction has sometimes been attacked, but it still stands as the most satisfactory method of analysis.

In the following experiments, what is known as the gelatine method has been used. This depends upon the fact that the tannate of gelatine is an insoluble compound and may easily be separated, dried, and weighed. A variation of this method that is perhaps an improvement is recommended and consists essentially in the use of hide powder in the place of gelatine. This was not tried

on account of the more extensive apparatus required.

In the preparation of the galls for the quantitative tests, the following steps were taken. Representative galls were chosen in every case, run through a mill until the product attained about the fineness of ground coffee, and finally thoroughly dried. From this product a weighed quantity was taken for analysis, from which an aqueous decoction was made by boiling briskly for half an hour. The decoction was then filtered, and enough water added through the filter to make the clear filtrate measure ablut 100cc for every gram of the crude drug in the portion taken for analysis. After heating this clear decoction to about 70°C, enough of the hot solution of the following was added to completely precipitate all the tannin present.

Gelatine	3gm.
Alum	2gm.

Disslove in 1,000 cc of boiling water.

The tannate of gelatine thus precipitated, collected on two counterpoised filter papers, dried, and weighed, forms the basis for the calculations as to the quantity of tannin present in the sample taken. It has been found by Johanson and others that fifty-four per cent of this precipitate of gelatine tannate is the weight of the tannic acid present in the compound, and therefore the weight of the acid present in the galls.

In pursuance of this method, the following exper-

iments were made with the tabulated results.

Sample 1.

These galls were a small dark globular variety found on the oak trees growing on a hillside west of Corvallis, and were of a hard, brittle texture.

Weight of sample	1.000 gm.
Weight of precipitate	.161 "
Weight of tannic acid (54% of precipitate)	.08694"
% of tannic acid	8.694 "

Sample 2.

These were the large spongy variety, or "Oak balls", as they are commonly called, and grow on the foothills west of Corvallis. They were in fair shape, not showing discoloration to any extent and were not mouldy.

Weight of sample	1.278 gm.
Weight of precipitate	.348 "
Weight of tannic acid	.18792 "
% of tannic acid	14.70

Duplicate

Weight of sample	1.278 gm.
Weight of precipitate	.34 "
Weight of tannic acid	.1836 "
% of tannic acid	14.34

Sample 3.

These leaf galls or "pop-balls" were obtained from the leaves of the oad and are very numerous in some localities. They are almost hollow, having only a rather firm out shell and a central part of stone cells held in place by numerous radiating threads.

Weight of sample	2.000 gm.
weight of precipitate	.2642 "
Weight of tannic acid	.1427 "
% of tannic acid	7.135

Duplicate

Weight of sample	2.000 gm.
Weight of precipitate	.318 "
weight of tannic acid	.17172 "
% of tannic acid	8.586.

Sample 4.

This sample consisted of powdered galls of unknown quality or variety bought at a local drug store.

Weight of sample	2.000 gm.
Weight of precipitate	.559 "
Weight of tannic acid	.302 "
% of tannic acid	15.09 "

Duplicate

Weight of sample	2.000n gm.
Weight of precipitate	..538 "
Weight of tannic acid	.291 "
% of tannic acid.	14.526 "

Sample 5.

These were small galls of the same variety as Sample 1, but were gathered in February, about a month later than the first specimens and were in a rather poor condition on account of the protracted rains having softened them.

Weight of sample	1.500 gm.
Weight of precipitate	.266 "
Weight of tannic acid	.14364 "
% of tannic acid	9.574

Duplicate.

Weight of sample	1.500 gm.
Weight of precipitate	.273 "
Weight of tannic acid	.14742 "
% of tannic acid	9.848

Sample 6.

This sample was of a peculiar wart like gall that

was found on only one group of trees growing near Mary's river.

Weight of sample	1.000 gm.
Weight of precipitate	.3625 "
Weight of tannic acid	.19575 "
% of tannic acid	19.575

Duplicate

Weight of sample	.8511 gm.
Weight of precipitate	.2747 "
Weight of tannic acid	.148338 "
% of tannic acid	17.418

Sample 8.

These were small galls of the same variety as Sample 1, but gathered from trees growing along Marys river.

Weight of sample	2.000 gm.
Weight of precipitate	.153 "
Weight of tannic acid	.08262 "
% of tannic acid	4.262

Sample 8.

Thissample is one from a collection of the large galls or "oak balls" that were gathered along Mary's river.

Weight of sample	3.000 gm.
Weight of precipitate	1.689 "
Weight of tannic acid	.91806 "
% of tannic acid.	30.602 "

Duplicate.

Weight of sample	3.000 gm
Weight of precipitate	1.827 "
Weight of tannic acid	.98658 "
% of tannic acid	32.886

Sample 9.

This is another sample of the small round galls gathered near "Old Baldy" and were in poor condition, being somewhat water soaked.

Weight of sample	3.000	gm.
Weight of precipitate	.271	"
Weight of tannic acid	.14634	"
% of tannic acid	4.88	

Duplicate.

Weight of samples	3.000	gm.
Weight of precipitate	.250	"
Weight of tannic acid	.135	"
% of tannic acid	4.5	

Sample 10.

This sample is from a few peculiar galls found only around "Old Baldy". They were about the size of a marble and were soft and spongy.

Weight of sample	2.000	gm.
Weight of precipitate	.260	"
Weight of tannic acid	.1404	"
% of tannic acid	7.02	

Sample 11.

This is the analysis of another sample of the powdered galls commonly found in drug stores and is of unknown kind or quality.

Weight of sample	3.000	gm.
Weight of precipitate	.513	"
Weight of tannic acid	.277	"
% of tannic acid	9.2	

Duplicate.

Weight of sample	3.000	gm.
Weight of precipitate	.5765	"
Weight of tannic acid	.3113	"
% of tannic acid	10.56	

By the predeeding experiments it will be seen that the large galls or "Oak Balls" are the only ones found in this portion of the Willamette Valley that contain enough tannic acid to deserve more thatn a passing notice.

These large galls, however, which contain as high as thirty per cent when gathered at the time of year when their tannic content is smallest, show a percentage almost on a par with those of the eastern parts of the United States, as well as those of Germany and France. Watson Smith, a English analyst, has published the following report of his work on the European galls mentioned above:

German galls	
Tannic acid	26.71%
Gallic acid	only traces.
French galls	
Tannic acid	24%

The galls near Philadelphia have been analyzed by the State Experiment Station, and 31.68% of tannic acid was found to be present; while from Texas comes the report of 40% having been found in some galls of that state which resemble the Aleppo galls. This is the highest per cent of di-gallic acid content reported as having been found in any North American nutgalls.

The same experiment station reported that the galls gathered after the maturity of the larvae always contained a great deal smaller per cent of tannic acid than those gathered earlier. In pursuance of this idea and also because the galls used in the above experiments were gathered at various times during the wet season and had consequently been soaked by the rains and were beginning to mould in places; experiments were tried for the detection of gallic acid, the decom-

position product of tannic acid. This acid would more likely be present in the galls on account of their water soaked condition than because of the fact that the larvae had long since developed and escaped, for it is obtained commercially from tannin by soaking the powdered galls in water for some time.

In the experiments, the filtrate from the precipitated gelatine tannate was taken for the analysis. The acid was precipitated as copper gallate by a solution of copper acetate, the precipitate filtered out and burned in a crusible to cupric oxide. In similar tests analysts have found that 90% of the weight of the cupric oxide represents the weight of gallic acid present.

In the experiments tried with several samples, gallic acid was shown to be present, representing as high as 16% of the crude drug in the case of Sample 9. Others showed almost as high a percentage, thus proving that the breaking down of tannin had occurred; for the report of such analysts as Watson Smith and Schiff show scarcely two per cent of the acid to be present normally and generally only a trace.

In order to determine the physical characteristics of the crude tannin obtainable from the large galls, an extraction of the powdered"oak balls" was made with eighty per cent ether as the menstrunm. Upon expression, after twenty-four hours maceration, the resulting

liquid divided into two portions a lower one of a thick consistency and deep brown color, and an upper ethereal portion that was sistinctly yellow. These were easily separated and each was slowly vaporated to dryness. The lower portion left a dark brown, friable, resinous mass that had no crystalline formation. It was the crude tannin, and responded to all the tests and reactions of the acid.

The upper portion crystallized upon evaporation into elongated crystals which were slightly yellow in color and decidedly acid in reaction when tested with litmus paper. An attempt to remove the vegetable coloring matter by shaking the ethereal solution of the acid in a separatory funnel with chloroform and water was successful to a great extent, and almost colorless elongated crystals were deposited on the sides of the vessal upon the second evaporation. This purified product in solution was subjected to an extended series of qualitative tests, resulting in identifying it as gallic acid. The quantity of gallic acid obtained by extracting the galls in this manner again points to the large percentage of the acid present in the samples and again indicates the breaking down of the tannin and the degeneration in quality of the galls.

In summing up the results of the above experiments, it may be said that they lack the quality of conclusive proof; yet they serve to indicate that at least one of

the galls commonly found on the Western oak is as good in quality as any found outside of the Orient and better than the powdered drug commonly sold in the drug stores. The specimens were gathered from six to seven months after they had reached their prime, and were probably greatly damaged by the deteriorating effects of the damp climate of this section of Oregon.

From the difficulties encountered during the course of these experiments, it would seem advisable to use some other system of determination than the gelatine method. Lowenthal's permanganate method, the one most extensively used in pharmaceutical determinations, has the advantage of speed and would probably show less variation in its results, the only disadvantage being that the standard solutions required contain a few materials not readily obtained, and thus, for a few determinations, some other method may be preferred to making the required solutions.

From this it will be seen that further research under more favorable conditions is needed to fully establish the quality of the Western Oregon nutgalls, and when due attention is given to their analysis it will probably be found that they rank well in comparison to those ofother sections of America and Europs, if not next in quality to those of the Orient, the Aleppo galls.

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