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TANNIN CONTENT OF ENGLISH WALNUTS

Thesis

Presented to

the Faculty of the Department of Chemistry

College of the Pacific

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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by

Joseph G. Natoli

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INTRODUCTION

Present methods for the production of leather from animal hides still depend for the most part on the use of natural tannin extracts. During the year, 1952, the amount of natural tannin extracts used by the leather industry was 560,452,119 pounds as compared to 35,793,000 pounds of synthetic tanning materials. It is not as yet possible to produce synthetic materials as economically as the natural extracts; the result being that there is still a very great demand for natural tannin extracts. The need for finding new domestic sources of tannins is apparent when the amounts of domestic and imported extracts are compared. During the period 1940-1950, only 744,394,560 pounds of natural tannin extracts were produced domestically as compared to 1,579,244,280 pounds of tannin extracts which were imported.

Tannins are known to occur in various parts of plants and they are also known to occur in the majority of the members of the plant kingdom.

The purpose of this research is to investigate the feasibility of utilizing parts of the walnut tree as a source of tannins.

THE OCCURRENCE AND PROPERTIES OF TANNINS

Occurrence of tannins. Tannins are complex organic compounds found naturally in varying degree in the majority of the members of the plant kingdom. The tannins found in plants vary in composition according to the species of plant from which it is extracted.

Various theories have been set forth to account for the presence of tannins in plants. According to one theory, tannins are thought to be the end product of metabolism since they often occur in the dead portions of the plant. Another theory holds that tannins are plant antiseptics because they occur in portions of plants which have been attacked by insects. As yet there is insufficient evidence to substantiate either theory.

With only one exception, the corn weevil tannins are found only in the plant kingdom.

Physical and chemical properties. Tannins are characterized by properties which vary according to the plant in which they occur. In general they have the following properties in common:

1. They are amorphous and very seldom crystalline.
2. They are weak acids.
3. They have an astringent taste.
4. Most tannins produce precipitates with alkaloids, however, there are exceptions as in the case of

gallotannin which has no effect on aconitine, berberine, betaine and other alkaloids.

5. They precipitate gelatin from solution.

6. They are soluble in water and in alcohol but they are insoluble in ether or benzene.

7. They are susceptible to fermentation leading to the formation of acids and sugars.

8. They contain phenolic groups.

9. They form precipitates with lead acetate and potassium dichromate.

10. They give color reactions with iron salts.

The difference in composition of tannins can be seen from the fact that their water solutions vary in color ranging from straw yellow to red.

Various classifications for tannins have been proposed, two of which are especially noteworthy. Perkin divided the tannins into three groups:

1. Those which contain depsides.

2. Those which are derived from ellagic acid.

3. Those which yield phlobaphene.

Freudenberg classified the tannins into two groups:

1. Those which can be hydrolyzed by acids and enzymes. This group consists of groups 1 and 2 of Perkin's classification.

2. Those which cannot be hydrolyzed by acids and enzymes. This group is the same as the phlobaphene yielding tannins.

Nierenstein, one of the foremost authorities on the subject of tannins, prefers the Freudenberg classification to which he has added a third group, the unclassified tannins.

CHARACTERISTICS OF THE WALNUT TREE

The walnut tree belongs to the Genus Juglans which is a member of the Family Juglandicae. The English or Persian walnut tree, Juglans regia, is the subject of this research. It is grown commercially in California and the southern states for the nuts which it produces. Through the years the wood of walnut trees has been highly prized for making veneer in the manufacture of furniture.

Originally the English walnut was imported from the European continent since its fruit is more desirable than the fruit of Juglans nigra, the Black walnut, and Juglans Californica, the California walnut, both of which are native to the North American Continent. The procedure used by California walnut growers is to graft English walnut stock on root stock of the Black walnut or of the California walnut.

The materials for this research were gathered from a tree growing in Modesto, California. They were collected from a tree approximately twenty years of age during the month of September, which is the walnut harvesting time.

The bark of the English walnut tree varies in color from grey for old bark to medium brown for the bark of new growth. The leaves are green color changing to brown during the autumn of the year. The husks are green in color during the spring of the year but the color changes to a dark brown by the time the walnuts are ready for harvest.

Only one report was found in the literature as to the tannin content of walnut trees. A European author reports the tannin content of walnut leaves as being 9 to 11%.

ANALYSIS PROCEDURE

The husks of ripened walnuts, green leaves, brown leaves, the bark of old growth, the bark of new growth and the bark of dead wood were collected during the month of September and were allowed to air dry for a period of five days. The samples were than ground until they could pass through a twenty mesh screen.

Extraction was carried out by two methods. The first method consisted of a modified soxlet unit as shown in the diagram (Figure 1). The unit was assembled from a 250 ml pyrex distilling flask to which a wider neck was attached so that the neck could accommodate an extraction thimble (25 x 100 mm). A glass tube was bent as indicated in the diagram and was attached near the base of the flask, the purpose being to be able to utilize nitrogen gas to circulate the extraction solvent through the extraction thimble. The solvent used was distilled water maintained at a temperature of 80°C. A 250 ml portion of distilled water was placed in the flask which was placed in a water bath maintained at 80°C. A ten gram sample of the material to be extracted was placed in the thimble and the water was circulated through it by adjusting the pressure of the nitrogen. The extraction was allowed to proceed for five hours after which the extracted material was transferred to a 1000 ml volumetric flask. A second 250 ml portion of water was placed in the

extraction unit and the extraction of the sample was continued for an additional three hours. The extract was combined with the first extract and the temperature of the combined extracts was allowed to come to room temperature. The volume of the extracts was brought to mark by the addition of water.

The second method of extraction consisted of leaching 10 grams of the material to be extracted with 250 ml of water in an Erlenmeyer flask placed in a water bath maintained at 80°C. A mechanical stirrer was used to keep the mixture agitated. The extraction was carried on for five hours after which the water extract was decanted into a 1000 ml volumetric flask and a second 250 ml portion of water was added to the residue. The extraction was continued for three hours. The second extract was combined with the first and allowed to come to room temperature. The volume was brought to mark by the addition of water.

ANALYSIS

Total solids: A 100 ml portion of the analysis solution was pipetted into an American Leather Chemists Association tared dish and evaporated to dryness on a hot plate maintained at 99°C. The evaporation and drying was carried out over a period of sixteen hours. The dish was weighed. The percentage of total solid was determined from the formula:

$$\frac{\text{Weight of residue times ten}}{\text{Weight of sample}} \times 100 = \% \text{ Total Solids}$$

Total soluble solids: Two grams of kaolin were added to a 225 ml portion of analysis solution and stirred until thoroughly mixed. The mixture was filtered through a 23.5 cm pleated filter paper so placed in a funnel so that the top edge of the filter paper was 1 cm below the rim of the funnel. After 40 ml had passed through, the filtrate was returned to the funnel. This procedure was continued for one hour. After an hour any liquid remaining in the funnel was removed by siphoning, care being taken so as not to disturb the layer of kaolin. A 225 ml portion of analysis solution was poured into the funnel. After 40 ml had passed through, the next 125 ml were collected. A 100 ml portion of this filtrated was pipetted into a tared dish, evaporated, dried, and weighed. The percentage of soluble solids was determined by the formula:

$$\frac{\text{Weight of residue times ten}}{\text{Weight of sample}} \times 100 = \% \text{ Soluble Solids}$$

Insoluble solids:

% Total solids less % soluble solids = % Insoluble Solids

Non tannin content: A 13.5 gram portion (equivalent to 12.5 g absolutely dry hide powder) was digested with 135 grams of water for .30 minutes after which 13.5 ml of 10% chrome alum solution were added. The mixture was agitated for two hours and allowed to stand overnight. The mixture was filtered through cheese cloth and squeezed until it

contained 73% water. The wet hide powder was digested with 180 ml of water for 15 minutes, filtered and squeezed, and repeated three additional times. To the wet hide powder 200 ml of analysis solution were added and the mixture was shaken for 10 minutes. It was then filtered through cheese cloth and the hide powder was squeezed lightly. The detanned solution was treated with 2 grams of kaolin and filtered as in the "Soluble Solid". Procedure: One hundred ml of clear detanned filtrate were pipetted into a tared dish, evaporated, dried and weighed. The percentage of non tannin was determined from the formula:

$$\frac{\text{Weight of residue (corrected for dilution)}}{\text{Weight of sample}} \times 10 \times 100 = \% \text{ Non tannin}$$

Normally the amounts of non reducing and reducing sugars would be determined. However, due to the low tannin contents found, the sugar determinations were not carried out.

TABLE I

DISTRIBUTION OF SOLIDS AND TANNINS

EXTRACTION BY MODIFIED SOXLET APPARATUS

	Husks	Green Leaves	Brown Leaves	Old Bark	New Bark	Dead Bark
% Total Solids	21.53	9.41	5.10	8.48	5.15	3.83
% Soluble Solids	19.40	9.05	4.48	6.96	4.60	3.11
% Insoluble Solids	2.13	.39	.62	1.52	.55	.72
% Non Tannin	13.04	5.18	2.51	3.51	3.38	1.64
% Tannin	6.36	3.87	1.97	3.35	1.22	1.67

TABLE II

DISTRIBUTION OF SOLIDS AND TANNINS

EXTRACTION BY LEACHING

	Husks	Green Leaves	Brown Leaves	Old Bark	New Bark	Dead Bark
% Total Solids	32.54	18.07	7.46	10.35	9.34	8.92
% Soluble Solids	30.23	15.40	5.36	8.84	7.61	6.05
% Insoluble Solids	2.31	3.67	2.10	1.51	1.73	2.87
% Non Tannin	21.73	8.84	3.08	5.41	5.47	4.43
% Tannin	8.50	7.46	2.28	3.43	1.14	1.62

SUMMARY

The English walnut tree is grown extensively in various parts of California for its fruit. The purpose of this research was to investigate the possibility of using parts of the walnut tree as a source of tannin.

To be commercially valuable, a natural material must contain at least 10% tannin. The results as tabulated in Tables I and II, indicate that none of the materials investigated approach this value to any significant extent.

BIBLIOGRAPHY

American Leather Chemists Association, Methods of Sampling and Analysis, 1946.

Bailey, L. H., The Standard Cyclopedia of Horticulture, Volume II; New York: The Macmillan Company, 1928, Pp. 3500-3505.

Brittan, N. L., North American Trees, New York: Henry Holt and Company, 1908, Pp. 215-220.

Dreaper, W. P., Allen's Commercial Organic Analysis, Volume V, London: P. Blakistan Sons and Company, Pp. 1-104.

Lewis, Squire and Broughton, Industrial Chemistry of Colloidal and Amorphous Materials; New York: The Macmillan Company, 1943, Pp. 383-389.

Nierenstein, M., The Natural Organic Tannin, Cleveland: Sherwood Press, 1934.

Encyclopedia of Chemical Technology, Volume XIII; New York: Interscience Encyclopedia Inc., 1954, Pp. 578-591.