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## Tannin content of certain California oaks

Arthur Carton  
*University of the Pacific*

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TANNIN CONTENT OF CERTAIN  
CALIFORNIA OAKS

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A Thesis  
Presented to  
the Faculty of the Department of Chemistry  
College of the Pacific

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In Partial Fulfillment  
of the Requirements for the Degree  
Master of Arts

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by  
Arthur Carton  
June 1952

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## TANNING

The converting of hides to leather can be traced to the beginning of civilization. In Genesis III, 21, one view of the first tanning is found where it is written, "Unto Adam and also his wife did the Lord God make clothing of skins and clothe them." Another view is that of pure speculation. Early man killed animals for food and probably at first discarded the hides; but after a time he used them for protective or decorative purposes. Man, by accident and observation, discovered the processes to keep the hides from putrifying and also to soften them for his use.

Evidence is available (Watson 1950) in museums that the Egyptians knew the art of tanning hides over four-thousand years ago. The Greeks and Romans knew not only the art of tanning but the art of coloring leather. The tanning processes of the late Roman era, with few modifications, were the same tanning processes practiced by modern tanners.

Methods used in the tanning of leather were not kept accurately until the guilds of the leather tanners were organized. One of the first guilds of this sort was established in Florence about 1098 and by 1238, the guild was one of the most powerful of the organizations. The monopoly on the art of tanning that Florence had was gradually broken by the other countries of Europe. Master tanners were induced to go to England, France, Spain, etc., until by the 16th century, the Florence guild had disappeared.

The method used by all of these countries was almost identical and is described by Edgecombe Stanley in his book, The Romance of Leather. He says:

The raw hides were first salted to check putrefaction, limed in weak lime liquor and brought to a suitable condition for dehairing and fleshing, within about three months. Then they were placed between layers of coarsely ground oak bark in pits until full, when a thick topping of bark was put over them. No water was used at this time. The packs were taken up and reversed several times, fresh oak bark being introduced. This kind of tanning occupied somewhere about 18 months....

The next process was 'handling', in which the hides were transferred to larger pits and then turned over every day in a liquid or ooze made of oak bark. This process lasted five or six weeks. If the skins were to be dyed it was introduced into this process. In later times, the skins were hung over big wooden bars immersed in the tanning dyeing medium.

From this description, the early tanning methods took almost two years to convert the hides to the finished product.

Tanning in the colonies and later the United States was confined to local tanneries that supplied only the local demand for leather. It was not until the turn of the 19th century, with the invention of the splitting machine by Samuel Parker in 1809, that tanning evolved from a local craft to a large scale manufacturing process. In 1840, Mellen Bray's invention of a fleshing and unhairing machine was one of the greatest contributions to modern tanning technique.

In 1878, the first chemist was employed in a tannery and by 1905 at least 150 tanneries employed leather chemists.

With the development of leather substitutes that are now appearing on the market, the leather chemists have a very important job. It is up to them to improve their product and lower prices in order to keep the tanning industry alive.

~~The supply of hides has never been a major problem~~ because they are a by-product of the food industry and as long as people eat meat, there will be hides to convert to leather. The supply of vegetable tanning agents is the one that could become critical. The majority of high tanning content materials are outside the United States and have to be imported. In order to become self-sufficient, extensive research has been carried out in the last few years to find commercially feasible supplies in the United States.

The purpose of this paper is to investigate three California oaks as possible sources of tannin. Even though the study of the three varieties of trees may not be representative samples, the procedures developed may prove to be valuable in a more extensive research by other workers.



## THE OAK TREES, A SOURCE OF TANNIN

The oaks form a large botanical group composed almost entirely of trees, some of which are the most important timber trees of North America. (Sudworth 1908). They are world-famous trees, which through their powerfully built trunks, branches, and roots, have earned the reputation of the greatest physical sturdiness. They grow rather slowly and require several centuries to produce the high-class saw timber which our first oak forests once furnished in great quantities; but which now is rapidly disappearing. They are world-wide and adapt themselves to dry non-reproducing soils, as well as to moist, fertile ones, and to cold as well as to warm climates. They prefer temperate regions, however. Their range is unlimited in that they may be found from near the sea to nearly 10,000 feet elevation in the mountains.

The two large classes of oaks--the white oak and the black oak--are more easily distinguished by the color of the wood. Technically, they are based upon different habits of producing acorns. The white oaks produce their acorns in one season; the black oaks produce theirs in two seasons.

Approximately 300 species of oaks are known in the world, 53 species of which occur within the boundaries of the Pacific region. All of these belong to California while one or two of them extend into the southern Rocky Mountain region.

## VALLEY OAK

*Quercus lobata* Née

Distinguishing Characteristics: Valley oak, so called because it grows chiefly in open valleys, is the largest of western oaks. (Sudsworth 1908). A prominent characteristic is its scattered presence. Huge short-trunked trees with broad round-topped crowns, grow naturally far apart. The large trunk with gray deep grooved bark gives off very large rough barked limbs at from eight to twenty-five feet from the ground, the lower branches sometimes dropping and reaching the ground. Some trees have tall trunks with small spreading short branches in a narrow crown; generally there is not more than a single length of clear saw timber in the trunk. Acorns which mature in one season are also variable in size and are produced in large quantities. The wood of the tree is dull brown in color; brittle, firm and difficult to work. Because of this, the tree is used more for fuel than for any other purpose.

## BLUE OAK

*Quercus douglasii*

Distinguishing Characteristics: This tree is the so-called "blue oak" because of the blue-green color of its

foliage, but known locally as "white oak" because of its light, ash-gray bark (Sudsworth 1908). Trunks exposed to the sun are especially light colored, sometimes even whitish, but are considerably darker gray in sheltered locations. The smooth-looking trunks are short and have no branches up to about ten or twenty feet. The branches are usually found to be bent and give off short, thick, horizontal twisted limbs. Acorns, are variable in size and mature in one season. The wood of this tree is dark mottled brown, very dense, heavy, stiff, and brittle, cross-grained, and difficult to work. Large trunks are often unsound. It is unfit for any commercial use but is good for fuel.

#### CALIFORNIA LIVE OAK

*Quercus agrifolia* Nee - *What the intention  
of the name? wood?*  
Hoot

Distinguishing Characteristics: The California Live Oak is one of the most common, best known of the southern California oak trees, as well as one of the first to attract the attention of early explorers, who called it, "holly-leaved oak", because of its resemblance to the large American or European evergreen holly (Sudsworth 1908).

Its trunk is short and bare and it has a narrow dome-shaped dense crown. It usually grows in the open uncrowded areas. Occasionally it is only a low shrubby tree. Long, thick, distorted limbs extend from the short clear trunk

which is often only four to eight feet tall. Trees in crowded areas have more slender branches. The smaller trees and the larger limbs of the big trees have a smooth light gray-brown bark with occasional ash-white areas. The large trees have thick, hard, black or very dark brown, rough and wrinkled bark with wide ridges.

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The foliage appears to be evergreen but remains on the trees only until the succeeding spring, usually falling before or a short time after the new leaves begin to form. The wood of this tree is brittle, hard, heavy, fine-grained, and reddish brown in color. Its only value is for fuel.

## TANNIN OCCURRENCE AND CHARACTERISTICS

### Occurrence of Tannins: (Griswold and Rogers 1941)

Tannin occurs in a large number of plants. The amount of tannin present in any plant may differ depending on the different parts of the plant analyzed. It is usually found in such dead parts of the plant as outer barks, some rinds, galls, etc., and is thought to be an end product of metabolism.

Tannin also occurs in the growing parts of the plant such as buds, immature fruits, root shoots, and inner bark. In general, tannins may be said to occur in vacuoles sep.

According to one theory, tannin exists in a plant because it is a so-called "plant antiseptic" and as such tends to prevent infection and attacks bugs, insects, and fungi. The reason for this theory may be that the tannin content increases if a plant is wounded.

### Physical and Chemical Properties: (Gortner 1949)

Tannin containing materials are widely distributed in nature and tannins may be characterized by the following properties:

1. Tannins are, generally speaking, amorphous and usually do not have crystalline forms.
2. Tannins have an astringent taste.
3. Tannins give colors with ferric salts (inks).
4. Lead acetate, potassium dichromate, and alkaloids precipitate tannin from solution.

5. Tannins precipitate gelatin from solution, which enables them to convert hides to leather.
6. Tannin solutions yield a deep red color with the addition of potassium ferricyanide.
7. Tannins are soluble in water to form a colloidal solution of the tannins.
8. Tannins all contain polyhydroxyphenols or derivatives of polyhydroxyphenols and in many cases, a complex condensed ring structure.
9. Tannins may act as a chromogen for oxidases.
10. When tannins are heated with dilute acids, insoluble amorphous anhydrides or phlobaphenes are produced.

It has been suggested that the tanning process may be regarded as the conversion of a relatively hydrophilic gel into a relatively non-hydrophilic gel which is called leather.

Not all tannins react the same chemically but they all have the same characteristic reactions because they all contain the phenolic groups. These groups in tannins are responsible for their color reactions with iron salts, their astringent action, their leather forming properties, and their precipitation with gelatin. Because of the antiseptic properties of phenolic groups, putrefaction is prevented from the tanning process.

It is beyond the scope of this paper to mention all of the work that has gone into determining the chemical and physical properties, structure and classification of tannins. A few of the important contributions will be presented. In 1867, Hlasiwetz (Nierenstein 1934) found that tannins contain the pyrogallol nucleus in addition to the nuclei of phloroglucinol and catechol. He classified the tannins into three groups: 1. The blue color in the presence of iron salts due to the pyrogallol nucleus; 2. The green color in the presence of iron salts due to the catechol nucleus; 3. The red color in the presence of pinewood and hydrochloric acid due to the phloroglucinol nucleus. Etti and Perkin found that this method of classification was not satisfactory in all cases but it was a beginning towards the proof of structure of tannins.

In 1918, Perkin divided the tannins into three groups: 1. The tannins which contain depsides. 2. The tannins which contained the diphenylmethylofid group - tannins derived from ellagic acid. 3. The tannins which yield phlobaphene. In this classification, group one gives a blue color with iron salts and groups two and three give a green color with iron salts.

In 1920, Freudenberg (Nierenstein 1934) classified tannins into two main groups: 1. The tannins that can be hydrolyzed by acids and enzymes; 2. The tannins that cannot be hydrolyzed by acids and enzymes.

According to Nierenstein, who in 1934 had been studying tannins for 30 years, Freudenberg's classification is the best and he adds only one other classification. This is "unclassified" tannins to which the oak tannins and the majority of the other tannins belong.

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## ANALYSIS OF OAK BARK

Preparation of Sample: The bark was collected from live trees and consisted of a strip approximately eighteen inches long and six inches wide extending vertically along the trunk of the tree. The bark slabs were air dried for two to three days and then ground so they would pass through a twenty-mesh screen. The bark was then ready for extraction.

Extraction: According to Snow and Bailey (J.A.L.C.S. 1949), 80° C. is the best temperature to obtain the highest extraction of tannin with the least impurities. With this fact in mind, extractions were not carried out by the conventional soxhlet extraction but were tried by two different methods: 1. extraction with the nitrogen bubble extractor; 2. extraction with the bark in the solution.

The nitrogen bubble extractor uses the air lift principle and was used because it resembles the soxhlet method of extraction with the exception that the temperature of the solvent can be kept at 80° C. and does not have to be at the boiling point of the solvent. The extractor and solvent were kept at 80° ± 1° C. by immersing the whole extractor in a constant temperature bath. Ten grams of the ground bark were put in a 25 x 80 millimeter extraction thimble and extracted continuously with 250 milliliters of water in the extractor. The extractions were carried out for one hour and two hours, respectively, with an extraction rate of 5 milliliters per minute.

The second method of extraction employed a 500 milliliter Erlenmeyer flask and a mechanical stirrer. This method was used to duplicate, as closely as possible in our laboratories, the method used in commercial extraction plants for the extraction of tannin. Ten grams of the ground bark and 250 milliliters of water were put into the 500 milliliter Erlenmeyer flask and then the flask was immersed in a constant temperature bath kept at  $80^{\circ} \pm 1^{\circ}$  C. The extractions were carried out for one and two hours, respectively.

Total Soluble and Insoluble Solids: (A.L.C.A. 1946)

After the extraction was complete, the liquid was transferred to a 250 milliliter volumetric flask, cooled, and brought up to the mark. A 100 milliliter portion of the liquid was pipetted into an American Leather Chemists Association tared dish and evaporated to dryness. The increase in weight of the dried dish represented the total solids. The hot plate used for this evaporation and all subsequent evaporations was maintained at a temperature between  $97^{\circ}$  -  $99^{\circ}$  C. The remaining 150 milliliters of extract were thoroughly mixed with two grams of kaolin and filtered through a fluted filter paper and returned until the filtrate was clear. A 100 milliliter sample of the clarified liquid was pipetted into a tared dish and evaporated to dryness. This gave the weight of the soluble solids. All of the insoluble materials were

filtered out by the action of the kaolin forming a very fine filter medium through which only the dissolved material could pass.

The difference between the weights of the total solids and the soluble solids gave the weight of the insoluble solids in the extract.

$$\frac{2.5x \text{ wt.}}{10g} \times 100 \% \text{ combined soluble solids and insoluble solids}$$

Non-tannin and Tannin: (A.L.C.A. 1946) 12.5 grams of American standard hide powder were digested, treated with chrome alum, and washed twice with water. The washed hide powder was squeezed through cheese cloth until the hide powder contained 73% water and was then added to 200 milliliters of the bark extract and shaken for ten minutes. The hide powder solution mixture was filtered through cheese cloth and squeezed lightly. Two grams of kaolin, to remove any insoluble material, were thoroughly mixed with the detanned solution and then filtered through fluted filter paper and returned until the filtrate was clear. A 100 milliliter sample of the clarified filtrate was pipetted into a tared dish and evaporated to dryness. The increase in weight times 2.84 gives the weight of the non-tannin material in the sample.

$$\frac{2.84 \times \text{wt.}}{10} \times 100 = \% \text{ non-tannin}$$

$$\begin{array}{r} \% \text{ soluble solids} \\ - \% \text{ non-tannin} \\ \hline \% \text{ tannin} \end{array}$$

Total Reducing & Non-reducing Sugars: (A.L.C.A. 1946)

A sample of 250 milliliters of the extract was shaken with 31.2 milliliters of a saturated normal lead acetate solution and let stand for ten minutes. The lead acetate precipitated the tannins completely and the solution was filtered through fluted filter paper. Usually 240 milliliters of filtrate were recovered and six grams of dried dipotassium phosphate ( $K_2HPO_4$ ) were added to remove the excess lead ion from the solution. The solution was filtered through fluted filter paper and returned until clear. Then 50 milliliters of the solution was pipetted into a 400 milliliter beaker and 25 milliliters of copper sulphate solution and 25 milliliters of alkaline tartarate solution (Fehlings A and B) were added by a pipette. The solution was heated to  $100^\circ C.$  in four minutes and held at this temperature for two minutes. It was filtered immediately through a tared gooch crucible, washed with hot water, washed with alcohol, and then with ether. The crucible was dried on a hot plate for one-half hour at  $97^\circ - 99^\circ C.$

Five times the weight of the  $\text{Cu}_2\text{O}$  gave the weight of  $\text{Cu}_2\text{O}$  produced by the reducing sugar in ten grams of bark. The  $\text{Cu}_2\text{O}$  is expressed as dextrose by use of the Munson & Walker table (Bulletin 107, Revised, Bureau of Chemistry, page 243).

To 150 milliliters of the original de-tanned solution were added 7.5 milliliters of concentrated HCl and refluxed for one hour. The solution was cooled and two drops of phenolphthalein were added and neutralized with saturated sodium hydroxide solution. If the end point was exceeded, the pink color was discharged by adding conc HCl a drop at a time. The neutralized solution was then transferred to a 200 milliliter volumetric flask and brought up to the mark. Then the  $\text{Cu}_2\text{O}$  was determined the same as in the reducing sugar section.

6.67 times the weight of  $\text{Cu}_2\text{O}$  gave the weight of  $\text{Cu}_2\text{O}$  produced by the total sugars in ten grams of bark. The  $\text{Cu}_2\text{O}$  was expressed as dextrose by use of Munson & Walker table (Bulletin 107, Revised, Bureau of Chemistry, p. 243).

Grams of total sugar  
- Grams of Reducing sugar  
Grams of non-reducing sugar

TABLE I

VALLEY OAK 80° C. N<sub>2</sub>

	One Hour	Two Hours
% Total Solids . . . . .	5.64%	3.95%
% Soluble Solids . . . . .	5.30%	3.26%
% Insoluble Solids . . . . .	.34%	.70%
% Tannin . . . . .	2.64%	1.08%
% Non-tannin . . . . .	2.67%	2.18%
Total Sugars . . . . .	.043 gm.	.038 gm.
Reducing Sugars . . . . .	.018 gm.	.023 gm.
Non-reducing Sugars . . . . .	.024 gm.	.015 gm.

TABLE II  
VALLEY OAK 80° C.

	One Hour	Two Hours
% Total Solids . . . . .	3.74%	4.78%
% Soluble Solids . . . . .	3.72%	4.36%
% Insoluble Solids . . . . .	.02%	.42%
% Tannin . . . . .	.48%	1.15%
% Non-tannin . . . . .	3.24%	3.21%
Total Sugars . . . . .	.052 gm.	.045 gm.
Reducing Sugars . . . . .	.026 gm.	.023 gm.
Non-reducing Sugars . . . . .	.027 gm.	.022 gm.

TABLE III

CALIFORNIA LIVE OAK 80° C. N<sub>2</sub>

	One Hour	Two Hours
% Total Solids . . . . .	13.52%	18.58%
% Soluble Solids . . . . .	12.96%	18.23%
% Insoluble Solids . . . . .	.56%	.35%
% Tannin . . . . .	5.86%	5.19%
% Non-tannin . . . . .	7.10%	13.04%
Total Sugars . . . . .	.701 gm.	.730 gm.
Reducing Sugars . . . . .	.436 gm.	.441 gm.
Non-reducing Sugars . . . . .	.265 gm.	.289 gm.



TABLE IV

CALIFORNIA LIVE OAK 80° C.

	One Hour	Two Hours
% Total Solids . . . . .	22.85%	22.39%
% Soluble Solids . . . . .	22.45%	19.57%
% Insoluble Solids . . . . .	.37%	.82%
% Tannin . . . . .	6.33%	4.01%
% Non-tannin . . . . .	16.12%	15.56%
Total Sugars . . . . .	.843 gm.	.839 gm.
Reducing Sugars . . . . .	.511 gm.	.524 gm.
Non-reducing Sugars . . . . .	.332 gm.	.315 gm.

TABLE V

BLUE OAK 80° C. N<sub>2</sub>

	One Hour	Two Hours
% Total Solids . . . . .	7.71%	7.48%
% Soluble Solids . . . . .	7.45%	6.88%
% Insoluble Solids . . . . .	.25%	.60%
% Tannin . . . . .	3.21%	2.59%
% Non-tannin . . . . .	4.25%	4.29%
Total Sugars . . . . .	.148 gm.	.142 gm.
Reducing Sugars . . . . .	.115 gm.	.104 gm.
Non-reducing Sugars . . . . .	.033 gm.	.038 gm.

TABLE VI

BLUE OAK 80° C.

	One Hour	Two Hours
% Total Solids . . . . .	8.35%	8.80%
% Soluble Solids . . . . .	7.68%	8.35%
% Insoluble Solids . . . . .	.67%	.45%
% Tannin . . . . .	3.40%	3.57%
% Non-tannin . . . . .	4.28%	4.78%
Total Sugars . . . . .	.157 gm.	.160 gm.
Reducing Sugars . . . . .	.121 gm.	.120 gm.
Non-reducing Sugars . . . . .	.036 gm.	.040 gm.

## SUMMARY

In the last few years, extensive research has been carried out in order to find new sources of vegetable tanning in the United States. The purpose of this paper is to help further the search by investigating three California oaks. This research is a part of a long-range research program on natural and synthetic tanning agents which has been instituted at this college.

The three California oaks which were investigated as possible sources of tannin are the Valley Oak, the Blue Oak, and the California Live Oak. The bark was collected from live trees, air dried and ground so it passed through a twenty-mesh screen. Extraction was carried out in two ways: 1. extraction with a nitrogen bubble extractor; 2. extraction with the bark in the solution. The extract was analyzed according to the American Leather Chemists Association, Methods of Sampling and Analysis 1946, with the following results: The Valley Oak had between 1% and 2.5% tannin; the California Live Oak had between 4% and 6% tannin; and the Blue Oak had between 2.5% and 3.5% tannin.

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BIBLIOGRAPHY

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## BIBLIOGRAPHY

- Gortner, Ross  
Outlines of Biochemistry  
John Wiley & Sons, Inc., New York, 1949.
- Griswold, O. and Rogers, C. H.  
The Chemistry of Plant Constituents  
Burgess Publishing Co., Minneapolis, Minn., 1941.
- Snow, F. A. and Bailey, L. F.  
The Journal of the American Leather Chemists Association  
Volume XLIV, No. 10, October 1949, 741, 742, 743 pp.
- Sudworth, George G.  
Forest Trees of the Pacific Slope  
U. S. Government Printing Office, U. S. Dept. of  
Agriculture, U. S. Forest Service.  
276 to 278; 285 to 288; 303, pp. 1908.
- Nierenstein, Maximilian, D. Sc.  
The Natural Organic Tannins  
Sherwood Press, Cleveland, Ohio, 16, 17, 18, 19, pp.  
1934.
- Watson, Merrill A. D. C. S.  
Economics of Cattlehide Leather Tanning  
Rumpf Publishing Co., Chicago, Ill., 3, 4, pp. 1950.
- Wilson, John Arthur  
The Chemistry of Leather Manufacture  
Chemists Catalog Co., Inc., New York, 1923.
- Weissberger, Arnold  
Technique of Organic Chemistry  
Interscience Publishers, Inc., New York,  
Volume III, 302, 303, pp. 1950.
- American Leather Chemists Association  
Methods of Sampling and Analysis  
1946.