

TANNIN – CLASSIFICATION, ANALYSIS AND APPLICATIONS

K.RAMAKRISHNAN and M.R.V.KRISHNAN

*Department of Chemical Engineering, Alagappa College of Technology, Anna University,
Madras – 600 025, India.*

Received: 10 March, 1994

Accepted: 30 March, 1994

ABSTRACT: *This article reviews the various aspects of tannin, which is finding varied uses in leather industry and pharmaceuticals.*

INTRODUCTION

Tannin, a chemical constituent derived from plant origin, has been known to mankind since ancient times. Till to-day, Lignin and tannin are considered to be “Dark Continents” of science as a lot of work is required to understand their complete nature. It is rather difficult to define the term “tannin” in a concise way as used in plant chemistry; it is generally used to include a whole group of substances (as in galls) having specific physical and chemical constituents which are responsible for transforming fresh hide into impermeable non-rotting leather. The definition of tannin has been enlarged to cover a whole mass of constituents which give general phenolic reactions. The essential property of tannin is the ability to combine with proteins and other polymers such as pectin.

CLASSIFICATION

Generally tannins are water soluble phenolic compounds; they have molecular weight in between 500-3000, giving the usual phenolic reactions and have the special properties such as ability to precipitate alkaloids, gelatin, and other proteins. It is classified in two groups, namely,

(a) Condensed type

(b) Hydrolysable type (Typical composition of some plant materials is given in Tables IV to VII).

(i) CONDENSED TANNIN :

This tannin is certainly more important than hydrolysable tannin; much less is known about their structure and many aspects are yet to be elucidated (8).

This type of tannin produces “tannin reds” while boiling with acid (1). Traditionally, most commercial sources of this type are heartwood of quebracho, bark of wattle. These have been used in leather process industries to get better types of quality leather.

(ii) HYDROLYSABLE TANNIN :

This is an ester of sugar and phenolic acids or their derivatives; the sugar is usually glucose, but in some cases polysaccharides have been identified (1,9). Acidic, basic or enzymatic hydrolysis often occurs spontaneously during extraction or purification (6). This type of tannin is further subdivided into ellagitannin and gallotannin.

(ii a) ELLAGITANNIN :

The ellagitannin is characterized by hexa hydroxyl diphenyl ester group besides polygalloyl esters. Ellagitannin yields ellagic acid on hydrolysis: in addition to other phenolic compounds, namely chebulic acid, chloroellagic acid etc. (1). Sources for ellagitannin are myrobalans, pomegranaterind, rose-apple etc.

(ii b) GALLOTANNIN:

Gallotannin is considered to be hydrolysable type since it yields gallic acid on hydrolysis.

The tannin is a complex polyphenolic substance which may be degraded easily. The following plant species contain gallotannin alone or mixed tannins, starch, sugar, etc : Myrobalan, Chinese galls, Turkish galls, Dhava, Sumach, Teri-pods etc.

The gallotannin, also called tannin acid, is obtained from plant galls. Turkish gallotannin occupies an important position amongst the vegetable tannins. The early workers (6,8) on this topic proved that it is a polygalloyl glucose derivative. Tannic acid isolated from its sources has a pronounced acidic reaction due to the presence of m-digallic and m-trigallic acid. It has the general physical and chemical properties such as precipitation of protein, gelatin astringent taste, blue-black colouration with ferric salts, forming leather with hides and absorption of oxygen from air. It dissolves readily in water, alcohol, ethylacetate but practically insoluble in ether, carbon disulphide and benzene (1). When it is boiled with acetic anhydride, it is converted into acetyl derivative, a crystalline, substance which melts at 137°C.

ANALYSIS

There are many methods suggested in the literature.

- (a) The tannin is treated with lead acetate and it is precipitated as lead gallo-tannate. This gallate is reacted with Hydrogen Sulphide, precipitated as copper gallate and then incinerated (7).
- (b) Tannic acid solution is treated with ferrous tartrate reagent after adjusting pH to 7; concentration can be analysed by spectro photometer at 540 nm (4).
- (c) Using Bovine – serum, the tannin is precipitated. It is then treated with SDS – Triethanolamine reagent; it is taken in the solution form and then analysed by spectrophotometer (5).

APPLICATION

TANNIN IN MEDICINE

Most of the Ayurveda, Siddha and Unani formulations like churna, Rasa, Bhasma, Khurs etc. contain many types of tannin as ingredients (2,3). A number of tannin bearing raw materials are used extensively in the preparation of folk and Indian medicines as indicated in Tables I, II & III. It is known that in folk medicine, the decoction of pomegranate-rind cures certain types of dysentery. Most of the ayurveda and siddha tooth powders contain tannin bearing materials to strengthen gums. The specific properties of tannin viz., ability to precipitate proteins and destroy most of the microorganisms have been exploited fully in Indian medicinal formulations. When a dilute solution of tannin is applied to a small open wound, it precipitates the protein of the

wound and forms a protective layers, thus preventing bleeding to help faster healing. Myrobalans, viz., chebulic (Kadukkai or Harda), Beliric (Thandrikkai or Bahead) and Embelic (Nellikai or Amla), Arjun bark, Chinese galls are some of the commonly used tannin raw materials for formulations (3). The mixture of the three myrobalan called “Triphala”, is claimed to cure some types of eye ailments and hence prescribed as a general tonic (Table I, II & III).

TANNIN IN LEATHER PROCESSING.

In leather industries, the art of tannin, i.e. converting animal hide or skin to leather is considered to be the first leather manufacturing process. Aqueous solution or infusions which contain Tannin (Known as tan liquors) of plant extract are colloidal in nature with a wide range of particle size. They are mixtures of polyphenols and high

molecular weight compounds. During tanning process, the collagen chains in the hide are cross-linked by tannin to give leather. The formation of various complex bonds help the tannin-protein polymer combination (8).

OTHER INDUSTRIES

Tannin or tannic acid finds application in ink manufacture, dye industry, plastic resins, water purification, manufacture of adhesives, surface coatings, manufacture of gallic acid etc.

CONCLUSION

The nature and composition of tannin vary from plant to plant and species to species. A lot of research in this field is very much needed to explore the utility and nature of the various types of tannin.

TABLE I

ITIINIFAL E SANA (UNANI) 2

S.No.	Ingredients	Amount
1	Chebulic myrobalan rind	15 gms
2	Beliric myrobalan rind	15 gms
3	Embelic myrobalan rind	15 gms
4	Senna Leaves	15 gms
5	Ghee	10 gms
6	Honey	150 gms

Action & Uses:

This drug is a purgative in large doses but laxative in small doses.

TABLE II
TRIPHALA CHURANA

S.No.	Ingredients	Amount
1	Chebulic myrobalan (without seed)	1 part
2	Embelic myrobalan (without seed)	1 part
3	Beliric myrobalan (without seed)	1 part

Action & Uses:

This churna is astringent, laxative and antibacterial, relieves Constipation. It is given in coughs with honey; in conjunctivitis, its decoction is used.

Used as a general tonic especially for eyes with equal quantity of honey and ghee. A dilute solution of this churna is used to wash and clean wounds and ulcer.

TABLE III
ASOKADI VATI (3)

S.No.	Ingredients	Amount
1	Asoka bark concentrated extract	500 gms
2	Calx of green vitriol	25 gms
3	Decoction of Asoka bark	100 gms

Action & Uses:

This table is a Haemostatic, astringent, uterine tonic and sedative.

TABLE IV
COMPOSITION OF SAL SEED

S.No.	Ingredients	Composition
1	Moisture and volatile matter	12.58%
2	Ash	3.63%
3	Crude Fat	2.24%
4	Crude Fibre	4.25%
5	Protein	12.13%
6	Sugar	5.18%
7	Starches	31.25%
8	Poly Sacchrides	3.51%
9	Tannin	13.6%
10	Unidentified	Rest

TABLE V
POMEGRANATE-RIND COMPOSITION (9)

S.No.	Ingredients	Amount
1	Moisture	8 – 12 %
2	Tannins	18 – 22 %
3	Soluble non tannin	16 – 23 %

TABLE VI
COMPOSITION ALEPPO GALLS (9)

S.No.	Ingredients	Composition
1	Tannin	65 %
2	Gallic Acid	2.0 %
3	Chlorophyll	0.7%
4	Gum	2.5%
5	Starch	2.0%
6	Fibre	15.68%
7	Moisture	12.0%
8	Unidentified	Rest

TABLE VII
CHEBULIC MYROBALAN

S.No.	Ingredients	Amount
1	Tannin	32 – 49 %
2	Non-Tannin	16.4 %
3	Ash	2.6 %
4	Gums	1.0 %
5	Fibre	Rest

REFERENCES

1. M. NIERENSTEN, D.Sc., "The Natural Organic Tannins", JCS Churchill Ltd., Portman Square, 108 – 150 (1934).
2. "Unani Pharmacopoeia" (Formulary of Union Medicines) IMCOPS, ADYAR, Madras 48, 49 (1982).
3. "Vaidya Yoga Ratnavalli" (Formulary of Ayurvedic Medicines) IMCOPS, ADYAR 93, 247 (1987).
4. "Methods of Test for Tannic acid" ISI 6897 – 1973.
5. Hangerman A.E., and L.G. Batler, Journal of Agricultural Food Chemistry, 26, 809 – 812 (1987).
6. Sadaaki Inbuchi, Yasuji Minoda and Koichi Yamada, "Studies of Tannic Acid Hydrolase of microorganisms" Agr. Biological chemistry 31, 5, 513 – 518 (1967).
7. Physico – chemical standards of Unani formulations part II central council for remedies in Unani Medicine (Ministry of Health and Welfare, Govt. of India, New Delhi 86, 87 (1987)).
8. E. Haslam chemistry of Vegetable Tannins Academic press London 82 – 92 (1966).
9. The Wealth of India Raw material series, CSIR New Delhi (1959).