VEGETABLE TANNING MATERIALS

HOWES

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Royal Botanic Gardens, Kew

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Early Boer settlers receiving seed of the newly established Australian Black Wattle from John Vanderplank, formerly a sea-faring man, at his farm—a favourite outspan—in the Midlands of Natal
From a painting by Peter Leftwich

By courtesy of the Director of the Wattle Research Institute, Pietermaritzburg, Natal

PREFACE

Tanning materials derived from plants have been used by man in many parts of the world from the earliest times for converting the skins of animals into leather or rendering them more suitable, more soft and more durable, for use as clothing and for other purposes. Tanning is in fact one of the oldest industries of the world and doubtless centuries ago, with some peoples, every man was his own tanner and tanned what skins he needed for himself and his family from the wild animals he slew. As mankind progressed and the tanning of hides and skins and the production of leather increased to become well-established industries, so did the demand and the use of vegetable tanning materials increase. With the development of world commerce, tanning materials came to be freely transported from one part of the world to another, often in very large quantities.

The progress that has been made in the tanning and leather industries, particularly during the last few decades, has called for changes in tanning technique and in the employment of the different kinds of vegetable tanning materials. In spite of the extensive use of mineral tanning substances (notably chrome tanning) and the interest in synthetic tans or 'syntans' that has existed for many years, vegetable tannins are still in demand and essential for many classes of leather, especially heavy leather and sole leather, so extensively used for footwear.

At one time the use of vegetable tannins by the tanner was very much more rigid than it is now. With the better understanding of the processes involved in tanning and the chemistry of tanning it is now possible to substitute one tanning material for another to produce the same type of leather. This is done by altering the chemical nature of the tan-liquor, *i.e.* by sulphiting and altering the degree of acidity or *p*H value of the tan-liquor or its salts or acids content. Among the major tans, for instance, wattle or mimosa may be modified to produce the same or similar results as chestnut, and chestnut in turn may be modified to produce similar results to quebracho. This was done on a large scale during the Second World War when the traditional tanning materials used in many countries became unobtainable, and it continues to be practised.

The world's need of tanning materials continues to increase especially with the increasing world population and the tendency for more and more of its people to wear boots and shoes. This applies perhaps with special emphasis to the peoples of Asia and Africa and some parts of the New World. Many feel that in the not-far-distant future there may well be a shortage of vegetable tanning materials for the world's leather industries, particularly in view of the decreasing supplies of two of the most extensively used tanning materials—chestnut (through disease) and quebracho from South America through the cutting out of the slow growing quebracho forests. The chestnut and quebracho industries formerly provided between them some 250,000 tons of tannin extract annually. It is also felt in some quarters that increased supplies of mimosa or black wattle may well be the most practical solution to these decreasing quebracho and chestnut supplies and that the world's rich potential supply of mangrove tannin might be more fully exploited, if certain difficulties such as high colour could be overcome, for extensive mangrove tracts occur throughout the tropics. It is due to considerations such as these that special attention has been given to both wattle and mangrove in this book.

Tannins are very widely distributed in the vegetable kingdom and the number of plants that contain tannin is legion. However, it is only those species that are rich or relatively rich in tannin that can be of interest as tanning materials. In this work an attempt has been made to deal at some length with all the important or commercial tans and more briefly with all those species known to be used in some part of the world in local or small-scale tanning but which do not enter world trade. With regard to tanniniferous plants not known to be actually used in tanning an attempt has been made (Chapter 41) to list all those species known to contain over 10% of tannin (dry weight) in some part or other of the plant, for it could be argued that such plants, or some of them, may one day be commercial tanning materials in their countries of origin. A few species, with a tannin content of less than 10%, have been included on account of special scientific or other interest that may be attached to them.

The importance of the tanning industry and of vegetable tanning materials may be judged from the fact that the annual importation of the latter (in crude and in extract form) to the United Kingdom alone is approximately a hundred thousand tons, and that the total annual production of vegetable tanned leather is about the same tonnage. The consumption of vegetable tanning materials in the United States is considerably larger and is believed to constitute about one third of total world consumption.

A word of explanation may be desirable in connection with the use of botanical names. As the average reader is not likely to be interested in the authority for the name but only in the plant itself the authorities for the names have been omitted purposely from the text. They are, however, available for those who may require them in the index of plant names at the end of the book. The families are also indicated in this index.

The writer is greatly indebted to the Director of the Royal Botanic Gardens, Kew, for the facilities afforded in carrying out this work, also to the British Leather Manufacturers' Research Association, the Colonial Products Advisory Bureau and to various other organizations and individuals who have kindly given assistance.

F. N. H.

Hanover House,
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1

INTRODUCTION

Nature of Tannin

The word *tannin* is generally used as a collective term for a whole group of complex substances that are of common occurrence and are widely distributed in the Vegetable Kingdom and which have certain characters in common. They are frequently and perhaps more appropriately referred to in the plural as the *tannins*.

It is not possible to give a clear or concise definition in chemical terms of the words tannin or tannins. In this respect the tannins are similar to other large and complex groups of plant products, such as the gums and resins, for they are equally difficult to define in concise terms. Tannins are complex organic structures, often with very large molecules and high molecular weights (to the order of 2,000 or more). They are built up from the elements carbon, hydrogen and oxygen. Some contain smaller amounts of other elements such as nitrogen and phosphorus. They were at one time classed with the glucosides on account of the sugar groups that most of them contain, but they are now generally regarded as constituting a class by themselves, for certain of them, *e.g.* the hemlock tannins, lack the sugar group in the molecule[140].

The tannins are mostly uncrystallizable colloidal substances with astringent properties and with the ability to precipitate gelatin from solution and to form insoluble compounds with gelatin-yielding tissues. It is this property which enables them to convert hides and skins into leather. The tannins are precipitated from solution by many metallic salts such as copper and lead acetates and by strong aqueous solutions of potassium bichromate or chromic acid. They give blackish-blue or blackish-green colours with iron salts, a property that has been made use of in ink manufacture, although other organic substances may give similar colour reactions.

Tannins are usually considered to consist of two main groups—the hydrolyzable tannins (pyrogallol group) and the condensed tannins (catechol group). Quite frequently the tannin, or tannins, extracted from a plant bears the characteristics of both groups and is actually a mixture of pyrogallol and catechol tannins. The hydrolyzable tannins may be hydrolyzed by acids or enzymes and include the gallotannins (from plant galls) and the ellagitannins which produce ' bloom ' on leather and which are characteristic of myrabolans, valonea, divi-divi and a number of other well-known tanning materials. The condensed or catechol tannins are not hydrolyzable and are characteristic of most of the important commercial tanning materials such as wattle or ' mimosa ', quebracho, mangrove and hemlock. They are more astringent (tan more rapidly) than the pyrogallol tannins, have larger molecules and are less well buffered. The catechol tannins yield less sediment, or lose less on standing but the leather often tends to turn a reddish colour on exposure to light. They yield phlobaphenes or ' reds '.

The chemistry of the tannins is still far from being well understood and is too involved for consideration in a book of this kind. An abridged survey of the chemical nature of the vegetable tannins has recently been made by ROTTSIEPER[153]. Others who have contributed to the subject in recent years or discussed it at some length are BERGMANN[31], FREUDENBERG[75], GNAMM[83], NIERENSTEIN[129] and PLATT[140].

Distribution of Tannin in the Vegetable Kingdom

The tannins may be said to occur throughout the greater part of the Vegetable Kingdom but to be more prevalent among the Angiosperms or higher plants, especially in certain Dicotyledon families, than they are among the lower organisms such as the Fungi, Algae, Mosses and Liverworts. The Ferns constitute an exception among the lower plants as tannin is sometimes very prevalent, the rhizomes of species of *Aspidium* having been recorded with tannin contents of 3—10% (dry weight)[57]. The Gymnosperms have classes in which tannin is well developed, familiar examples being the Pines (*Pinus*), Spruces (*Picea*) and Hemlocks (*Tsuga*). The Monocotyledons are poorly represented in species rich in tannin, many families and genera being normally devoid of tannin. The palm family (*Palmae*) however affords an exception and tannin is well developed in some species such as the date palm (*Phoenix dactylifera*), betel palm (*Areca catechu*) and North American saw palmetto (*Serenoa serrulata*).

Among the Dicotyledons there are many families in which tannin occurs very freely, the most notable being perhaps the *Leguminosae* (*e.g.* black wattle), *Anacardiaceae* (*e.g.* quebracho and sumac), *Combretaceae* (*e.g.* myrabolan), *Rhizophoraceae* (*e.g.* mangroves), *Myrtaceae* (*e.g.* Eucalyptus) and *Polygonaceae* (*e.g.* canaigre). Other families in which cells with tannin or tanniferous contents are common include the *Ampelidaceae*, *Annonaceae*, *Caryocaraceae*, *Celastraceae*, *Crassulaceae*, *Ebenaceae*, *Epacridaceae*, *Ericaceae*, *Geraniaceae*, *Lecythidaceae*, *Loranthaceae*, *Myricaceae*, *Myrtaceae*, *Plumbaginaceae*, *Proteaceae*, *Rhamnaceae*, *Rosaceae*, *Saxifragaceae*, *Sterculiaceae*, *Tamaricaceae* and *Vaccinaceae*[124].

In many families tannin occurs in some genera and species but not in others, as in the *Ranunculaceae* and *Rubiaceae*. There are also certain families in which tannin is absent or comparatively rare such as the *Gramineae* (grasses), *Cruciferae* and *Papaveraceae*[57]. The family *Myristicaceae* (to which the nutmeg belongs) is of special interest on account of the distinctive tanniferous tubes that occur in the rays of the wood of all species. As far as is known this type of tannin tube does not occur in any other family[124].

Plants rich in tannin occur both in temperate and in tropical or subtropical climates. Most of the commercially-important tanning materials such as wattle, quebracho, myrabolan, mangrove *etc* are products of warm countries. According to figures given by McNair[117], there are probably about twice as many species containing appreciable amounts of tannin in the tropics than there are in the temperate zone.

Tannins are usually regarded as restricted to the Vegetable Kingdom. It is of interest to note however that a tannin or tannin-like substance, giving all the usual reactions of vegetable tannins, has been described as present in the corn weevil (*Calandria granaria*)[129]. Possibly tannin-containing food materials may have had a bearing on the presence of the tannin or tannin-like substance in the insect.

Occurrence and Function of Tannin in the Plant

Tannin may occur in almost any part of a plant—root, stem or trunk, bark, leaves, fruit and even hairs. It may occur either in isolated individual cells, in groups or chains of cells (the more common method), or in special cavities or sacs. It may also be present in latex vessels and lactiferous tissue accompanied by other substances.

In living plant tissue, tannin is present chiefly in solution in the vacuoles. As the cell ages and loses its protoplasmic contents, the tannin commonly becomes absorbed in the cell wall. In dead tissue, tannin often accumulates in considerable quantity.

Tannins often occur freely in green or immature fruits, but the quantity decreases as the fruit ripens. They may also occur in seeds, often becoming more abundant after germination. Certain special plant structures may be rich in tannin, particularly those associated with movement. Tannin is often to be found in gland cells and the cells of pulvini (swollen leaf stalk bases). It is also very prevalent in the tissue caused through pathological conditions, *e.g.* in plant galls. Certain plant galls constitute the richest sources of tannin in the Vegetable Kingdom and are well-known commercial sources of tannin (see Chapters 37—40). The young, actively-growing tissue of plants is also liable to be very rich in tannin. An outstanding example is afforded by ‘ Dhawa sumac ’ (*Anogeissus latifolia*), for the young, red leaves and twigs of this Indian tree, when dried, may contain 50% tannin (see Chapter 32). However, in general, the highest concentration of tannin in normal healthy plants is commonly to be found in the bark.

The function of tannin in the plant or its physiological significance and its role in the metabolism of the plant is not well understood and has been the subject of much discussion. The same applies to certain other substances commonly found in plant tissue such as alkaloids, resins and gums. The general opinion now seems to be that tannin may serve several different functions and that its main function in one plant or group of plants may differ from that in another. It may be little more than a by-product in some plants but useful in others.

At one time teleological reasons were put forward to explain the presence of tannin. It was contended that the presence of tannin in leaves and green tissue would, owing to its astringency, prevent damage from browsing animals or other creatures and that it thereby served a protective role in the plant. Its presence in quantity in green fruits but not in ripe fruits, which commonly applies, was explained by stating that it was not in the interests of the plant that its immature or green fruits should be eaten, but that in eating ripe fruits animals often assisted in seed dispersal. It is sometimes contended that the presence of tannin in the epidermal or surface layers of leaves and shoots in temperate plants assists in resisting frost and that this may be the reason why many temperate evergreen plants have tannin well developed in their leaf tissue[117].

Tannin or solutions of tannin are known to be toxic to many plants. Concentrations of tannin as low as 0·1% and 0·8% have been shown to retard the growth of a large number of parasitic fungi[113]. The spores of some fungi will not germinate in media containing more than 0·6% tannin[24]. Some consider that one of the functions of tannin in the plant may be to assist in preventing infection by parasitic fungi when wounding or damage to the plant has taken place.

In more recent years the belief has grown that tannins may play some part in the formation of cork or corky tissue, that they may be intermediate products in the formation of cork tissue. Tannin is often very prevalent in bark which is the part of the plant where cork tissue is most freely developed. By treating cork in various ways decomposition products which show tannin-like properties have been obtained. Furthermore by passing carbon dioxide through mixtures of formaldehyde with tannins cork-like substances have been produced[139].

Tannins may play some part in the development of colour and pigmentation in plants. They show similarity in structure with the anthocyanin pigments. It is thought the disappearance of tannin during the ripening processes of fruits may be connected in some instances with the development of red, blue and yellow pigments so characteristic of ripe fruits[139].

The fact that young or immature fruits are frequently rich in tannin and that on ripening the tannin disappears or becomes much reduced in quantity or modified is of some importance economically for it applies to several everyday fruits such as the persimmon, the banana and the plum. In the persimmon, tannin is present in quantity in the unripe fruit, which is very astringent. On the ripening of the fruit, the tannin is considered to enter into combination with a colloid of a carbohydrate nature producing an insoluble gel, in which form the tannin is no longer astringent, or there may be a 'walling-off' of the tannin by a non-astringent layer. This process may be artificially stimulated in partially ripe persimmons by treating them with carbon dioxide and this is now a common commercial practice in some countries where persimmons are cultivated[139].

In the green banana, tannin occurs freely in the skin and the flesh. In the flesh, it is to be found mainly in the latex vessels which ramify through the flesh. On the ripening of the fruit these vessels lose moisture and their contents coagulate presenting a caked or cracked appearance under the microscope. This change is accompanied by the loss or lessening of astringency. In diseased or chilled bananas, the usual changes in ripening do not follow the normal course and hence their inferior edible qualities.

The tannin present in the flesh of a green banana may exceed 8%, while the flesh of a similar banana in the ripe condition may contain less than 2%. Similarly the skin of a green banana may contain 30—40% tannin and that of a ripe banana only 4—5%[24].