THE CHEMISTRY OF TEA MANUFACTURE

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The chemical changes that occur in the various stages of tea manufacture were, until recently, imperfectly known. Research in this direction would help not only in improving the existing methods of manufacture, but also in the solution of any fresh problems as they arise. In order to render the present manufacturing practices scientific rather than empirical, a thorough knowledge of the chemical and physical changes that take place during the various stages of its manufacture is very essential. The chief constituents of tea are, caffeine, tea catechins, pectins, proteins, carbohydrates, leaf pigments, vitamins, essential oils and mineral matter. Our present knowledge of these constituents of tea and the changes that they undergo during the processing of tea is briefly summarised in this article.

Caffeine

One of the principle constituents of tea leaf is the alkaloid caffeine which is a tasteless substance accounting for about 3-4 per cent of the dry matter. This alkaloid is also present in other vegetable sources like coffee, cocoa, cola, etc. About 80 per cent of the caffeine in black tea is soluble in the five-minutes brew. Nearly 60 per cent of the soluble nitrogen in tea is derived from this constituent. Caffeine does not undergo any change during the processing of black tea from green leaf. During firing, partial sublimation takes place and a very little of it is deposited on the roof of the driers.

Tea Catechins

Tea catechins are the most important constituents of tea and are responsible for the colour, pungency and characteristic taste of tea liquors. In the green leaf they are colourless, water-soluble compounds and constitute between 20 to 30 per cent of the dry matter. Until recently very little was known about their composition. Tea catechins (or tea polyphenols) are quite distinct from the substances used in the leather industry, such as oak gall tannin or tannic acid, which are powerful protein precipitants. The tea catechins are sometimes referred to as gallotannins. Much harm has been done as a result of the confusion of these two distinct groups of tannins so far as it concerns the effects of tea tannin on the human system. Tea catechins are quite harmless in this respect. A number of tea catechins have been separated into individual pure substances and their identity established. The most important of these are catechin, epicatechin, gallocatechin, epigallocatechin, epicatechin gallate and epigallocatechin gallate. Of these, it has recently been shown by Roberts* that the last three, and particularly epigallocatechin gallate are present in greatest amounts in tea.

Fermentation of tea was, for a long time, considered to be due to microbial activity, but recent research has established beyond doubt that it is caused by enzymic reactions of an oxidase (oxidizing enzyme) present in the green leaf. It is

* Roberts, E. A. H., (1958). J. Sci. Food Agric., 9, 381.

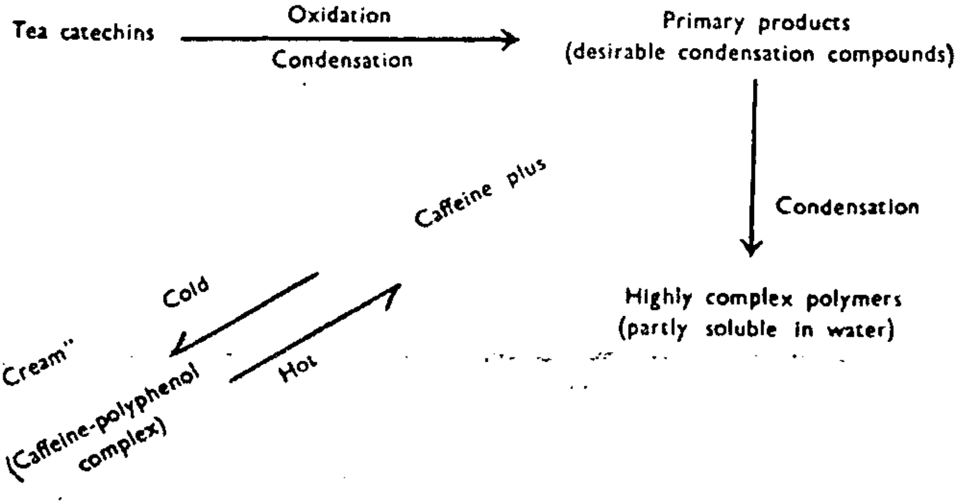
common knowledge that when an apple or a potato is cut and exposed to air, the cut portion assumes a brownish colouration after some time. On the other hand, if the potato or apple is dipped in boiling water before cutting discolouration is inhibited or at least very greatly retarded. This discolouration is due to the presence of oxidising enzymes in the fresh product which is sensitive to heat. A similar reaction occurs when tea leaf is ruptured in the rolling process.

Tea catechins, like most other polyphenolic compounds, have a large potential capacity for absorbing atmospheric oxygen and thus becoming oxidised. For this reason the polyphenol pyrogallol, which absorbs oxygen completely, is actually used for the determination of oxygen in mixtures containing the gas. But the absorption of atmospheric oxygen by tea polyphenols is normally very slow. In the presence of enzymes (biological catalysts) present in tea leaf, however, the rate of oxidation is very rapid. The tea catechins and the oxidising enzymes are present in different parts of the leaf cell; consequently, as long as the leaf is undamaged oxidation of the catechins does not take place. However, oxidation commences in leaf damaged during transit from field to factory, forming dark brown streaks at the site of the bruise.

Tea catechins do not appear to undergo any change during withering. The biochemical changes actually commence in the rolling process, one of the main functions of which is to rupture the cells of the leaf and to wring the leaf juices out of it. The catechins come into contact with the oxidising enzymes and start absorbing oxygen rapidly from the air and become oxidised. Some of the oxidised catechins polymerise almost instantaneously and then condense to assume gradully the characteristic coppery reddish-brown appearance of the fermented material. In other words, the oxidised molecules of tea catechins rearrange themselves and join together in this process. The oxidised catechins do also oxidise part of the green pigment of the leaf chlorophyll. These biochemical changes are allowed to continue during the process of fermentation until the optimum degree of colouration is obtained.

One of the chief functions of the next process in tea manufacture, namely, firing, is to arrest the enzymic reactions of the fermenting leaf. Enzymes in general are very sensitive to heat treatment and their activity is completely destroyed at high temperatures. This property is made use of in the manufacture of green tea where the leaf is subjected to a process of steaming prior to its manufacture. Tea enzymes are destroyed as soon as the fermenting leaf is subjected to the high temperature of the driers. The moisture content of the product is reduced to about 3-4 per cent from about 50-60 per cent in the fermented material before firing.

The products of condensation of tea catechins present in made tea may be grouped into: (*a*) water soluble and (*b*) water insoluble constituents. The water soluble products may be further divided into (i) ethyl acetate soluble and (ii) ethyl acetate insoluble fractions. The *desirable* characteristics of tea liquors are derived mostly from that fraction which is soluble both in water as well as ethyl acetate. Roberts (*loc cit*) has recently shown that the colour of tea liquors is due to two groups of pigments (1) thearubigins which are rusty brown in colour, acidic in nature and constituting about a third of the dry matter of the extract, and (2) theaflavins which are golden yellow in colour, neutral in reaction and constituting about 6 per cent of the soluble matter. These are reported to bear a close relationship to the quality of tea. The ethyl acetate fraction combines with caffeine to form a loosely held complex which precipitates when the liquor cools down. Tea tasters term this phenomenon "creaming down" and part of their evaluation of teas depends on the amount of this "cream." The scheme of reactions that take place in the fermentation of tea catechins and the formation of the "cream" may be represented as follows:



In under-fermented and over-fermented teas, the primary products are present in lower amounts than in normal teas with consequent effects on creaming.

Pectic Substances

Pectic substances which chiefly include pectin and pectic acid account for nearly 4 to 6 per cent of the dry matter in tea. They are invariably present in all fruits and vegetable sources, but citrus rind is a particularly rich source of pectin. Pectic acid has the property of forming a gel in acidic media and this property is made use of in the manufacture of jams and jellies.

Tea pectins are partly broken down into pectic acid and methyl alcohol in the presence of another enzyme, pectase, or more correctly, the tea pectin methyl esterase. Damage to, or bruising of the leaf, during rolling starts this reaction as well which also continues during the process of fermentation. The reaction is arrested by the high temperatures at firing.

The tea pectin-pectin methyl esterase reaction appears to control the tea polyphenol-polyphenol oxidase reaction of the fermenting material to a large extent. The pectic acid formed in this reaction appears to form a gel in the acidic fermenting material which coats the surface of the latter. Such a gel coating impedes the free absorption of oxygen by the tea catechins and slows down the oxidative process. It also appears that the pectic acid gel helps in the retention of the characteristic twist assumed by the leaf during the rolling process.

Most of the methyl alcohol produced in the reaction is lost into the atmosphere, but it appears likely that part of it is held back by the leaf tissues and possibly converted into esters by combination with the organic acids of the leaf in the presence of an esterifying enzyme. The flavouring constituents of many food products are mostly esters.

Essential Oils

The essential oils of tea are mostly methyl esters of various organic acids and are present in exceedingly small quantities. Japanese workers obtained about half an ounce of these oils from about one thousand pounds of tea.

Chlorophyll and Other Pigments

It has been stated earlier that the oxidised catechins of tea in their turn oxidise part of the chlorophyll pigment of the leaf causing the disappearance of the greenish colour of the mass during fermentation. Part of the chlorophyll is also decomposed during firing. No change appears to occur to the carotenoid pigments during the various stages of manufacture.

Carbohydrates

The amount of carbohydrates in tea leaf is extremely small. These substances are broken down to water and carbon dioxide by the respiring leaf to provide the necessary energy for cellular activities. Respiration continues throughout withering and even during rolling and fermentation *undamaged leaf* continues to respire to some extent. It has been found that 1 to 2 per cent of the dry matter of the leaf is lost on account of respiration during withering.

Proteins

Tea contains minute quantities of proteins and amino-acids. Proteins are partly broken down to simple water soluble substances, the amino-acids, during withering. They do not appear to have any role in fermentation, nor do they appear to undergo any further change during the process of manufacture.

Vitamins

Tea leaf contains carotene (pro-vitamin A), ascorbic acid (vitamin C), and the vitamins of the B group riboflavin, thiamine and pantothenic acid. Carotene being insoluble in water is not found in the beverage, whilst vitamin C is completely destroyed during tea manufacture. The vitamins of the B group are not affected by the manufacturing process and are highly soluble in water. It has been found that a cup of tea contains about 27 ug riboflavin and 75 ug pantothenic acid. About 5 cups of tea provide nearly 5 per cent of our daily requirement of these vitamins.

Minor Elements

Tea contains minute quantities of copper, zinc, boron, aluminium, iron, calcium, manganese, magnesium and fluorine. Copper forms an essential part of the polyphenol oxidase and is therefore of vital importance for the fermentation of tea. About 25 per cent of the copper content of tea leaf is present in the enzyme system. This discovery was put into practical use in Nyasaland where it was found that teas grown in certain areas could not be fermented properly until they were sprayed with copper compounds. Their soils were found to be deficient in this element.

During the spraying of tea with copper fungicides for the control of blister blight it has been found that part of the residual copper is absorbed by the leaf and retained to some extent. When applied in great excess copper replaces some of the magnesium in the chlorophyll molecule, and the copper-chlorophyll formed being more resistant to oxidation by oxidised tea catechins than normal chlorophyll, leads to the production of greenish infusions. It should be mentioned however that greenish infusions are also the result of under-fermentation of tea leaf. Up to 20 per cent of the copper in tea is soluble in the brew. Minute quantities of copper are essential in the human diet for the normal functioning of the liver in the formation of blood.

Tea contains traces of fluorine part of which is soluble in water. It has been found that drinking water containing traces of fluorine is beneficial for the healthy growth of teeth and in the prevention of dental caries. The liquors from Ceylon teas can, therefore, be considered to have a possible beneficial effect for this reason.