TEA FERMENTATION.—Part I.

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INTRODUCTION.

When withered tea leaf is rolled and then spread in layers in the atmosphere it loses its green colour and assumes a coppery tinge, while the fresh smell gradually changes to the well known aroma of undried tea. The property of changing colour and developing a characteristic aroma is made use of in determining when the leaf is ready for firing, but any standard based on such observations is essentially of an arbitrary nature and will vary with different observers. At the same time certain components of the leaf are transformed in such a way that the liquors obtained on infusing the tea gain in strength and colour. The greenish tinge observed in the liquors of fresh or withered leaf seems to disappear and red coppery liquors are obtained. This change is accompanied by a loss of pungency and briskness and the appearance of the liquors and of the infused leaf, combined with the taste of the liquors, may be taken as a criterion of the extent to which these changes have taken place during the manufacture. These transformations are generally known as tea fermentation and this process of tea manufacture is carried out according to certain arbitrary standards based on visual and sensory judgments of the changes described. A qualified success has been obtained this way, but a proper control of the process cannot be hoped for until a good deal more is known about the chemical changes which take place in the leaf and the factors which control or modify these metamorphoses. The problem of the control of fermentation will not be solved either by isolated factory or laboratory investigations, but requires a combined study under factory and laboratory conditions. In spite of an ignorance of the true nature of tea fermentation, a certain amount of excellent work has been done on the question in various countries and this serves as a stepping stone for further work. Since some of this work is reported in foreign journals and therefore inaccessible to many people on account of linguistic difficulties, it is proposed to give a short account of these investigations in these articles.

OXYGEN REQUIREMENT OF FERMENTING LEAF.

The fermenting tea leaf requires oxygen if those chemical changes which produce black tea are to take place, *i.e.*, one important process in tea manufacture is the oxidation of some component of the leaf. This was demonstrated in several ways by Bamber (*Chemistry & Agriculture of Tea*, 1893, 227), who showed that freshly-rolled leaf will remain green when placed in a vacuum or under an inert gas like carbon dioxide. He found that the air in contact with the rolled leaf could be replaced by pure oxygen without

detriment to the fermentation, and naturally came to the conclusion that a supply of oxygen or air was essential. The amount of oxygen used up by the leaf during fermentation was measured by Mann (*The Fermentation of Tea.* 1907, Pt. II., 11) who found that on the average 4½ pounds of fermenting leaf exhausted the oxygen from one cubic foot of air. Bosscha and Brzeskowsky (*Med. v. Proefstation v. Thee,* 1916, 47) found that the utilisation of oxygen by the leaf was accompanied by the production of carbon dioxide and record the following figures from one of their experiments in which they analysed the air in contact with the fermenting leaf for carbon dioxide and oxygen:—

	C.C. CO_2		C.C. CO_2
50 cc. of air at the beginning of the experiment	0·1	...	10·0
	0·15	...	9·9
50 cc. of air at the end of the experiment	8·2	...	0
	8·5	...	0

They observed that the flask in which the fermenting leaf was placed did not contain enough oxygen to complete the fermentation of 200 gms. of leaf which remained greenish until the flask was opened, when the leaf quickly attained the normal coppery colour. If rolled or crushed leaf was allowed to lie in a current of pure hydrogen, carbon dioxide or nitrogen, it remained green and did not show any sign of fermenting.

The absorption of oxygen with the production of carbon dioxide is characteristic of respiration in plants and animals, and the tea leaf is no exception to this. I have measured the respiration of the tea leaf at 18°C in a crude way and found that 40 gms. of fresh leaf produced 13.9 c.c. of carbon dioxide in one hour and absorbed 17.4 c.c. of oxygen in doing so. This gives a value of 0.8 for the ratio CO_2/O_2 for fresh leaf. The respiration decreases as the leaf loses moisture during withering, and 40 gms. of withered leaf only produced 9.8 c.c. of carbon dioxide in one hour. The volume of oxygen used up by the same leaf was 11.0 c.c. so that the ratio, $CO_2/O_2 = 0.98$, is a little higher but still of the same order. When the leaf was crushed, however, 40 gms. of leaf produced 3.4 c.c. of carbon dioxide, but at the same time absorbed 26.0 c.c. of oxygen. The oxygen uptake of crushed withered leaf is therefore considerably greater than that of uncrushed leaf, and the ratio, $CO_2/O_2 = 0.13$, is therefore of a very different order from that for fresh or withered leaf. The respiratory process is therefore upset when the withered leaf is crushed, and during fermentation the normal process of respiration is not observed. The utilisation of oxygen by crushed leaf proceeds rapidly for the first 3-4 hours and then slows down as will be seen from Fig. I. This is in keeping with observations of the rate at which fermentation proceeds in the factory

and further supports the contention that oxygen is essential for tea fermentation. The important rôle played by the oxygen of the air in tea manufacture thus makes it necessary to have a proper system of ventilation in the fermenting room so as to remove any carbon dioxide which accumulates as a result of the respiration of the leaf, and to supply plenty of oxygen for the oxidative changes.

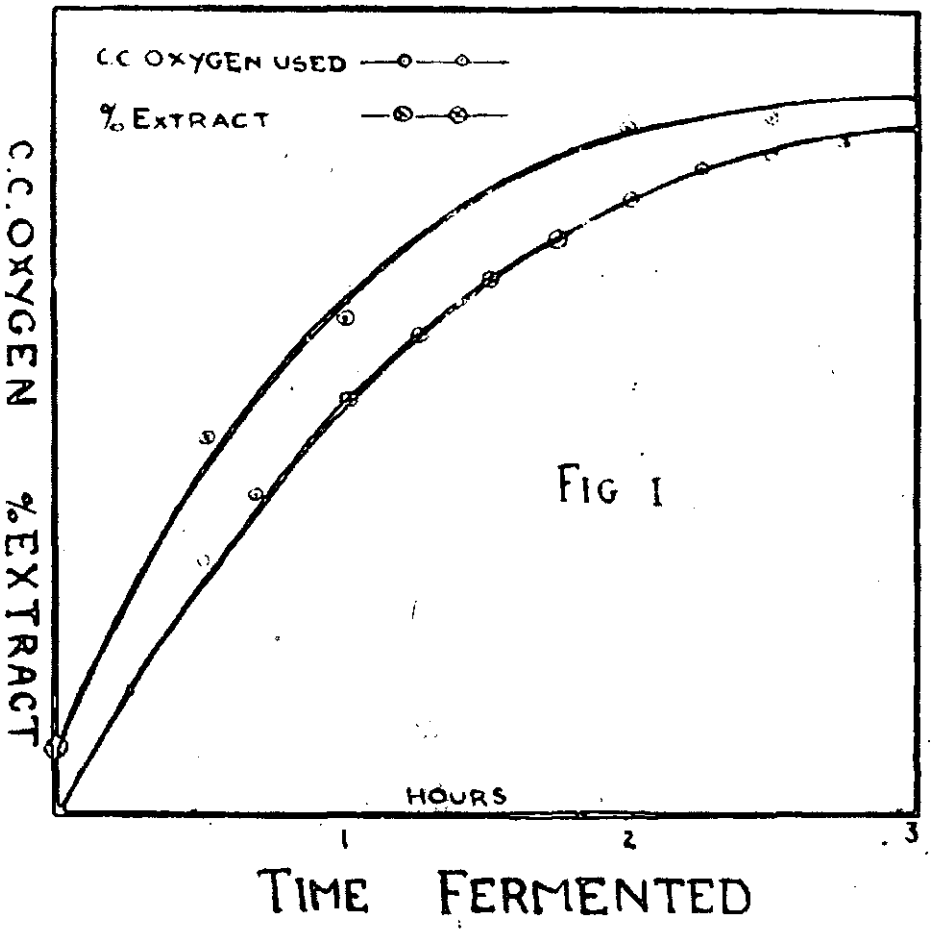

FIG 1

CHEMICAL CHANGES OBSERVED DURING FERMENTATION.

The oxidative process is accompanied by certain changes in the soluble constituents of the leaf, and these changes have been studied by several workers by comparing the chemical composition of the made tea with that of fresh leaf and green tea. Any difference in composition of the made tea from that of fresh leaf is

then attributed to fermentation. Kozai found the following differences between the green leaf and the black tea made from the same leaf:—

Elements.	Percentages. In dry leaf.	In black tea.
Crude protein ...	37·33	38·90
Fibre ...	10·44	10·27
Extracted by ether ...	6·49	5·82
Other non-nitrogenous extract ...	27·86	35·39
Ash ...	4·97	4·93
Caffeine ...	3·30	3·30
Tannin ...	12·91	4·89
Water-soluble material ...	50·97	47·23
Total nitrogen ...	5·97	6·22
Albumin ...	4·11	4·11
Starch ...	0·91	0·12

On examining the above table, it will be seen that it is the tannin which undergoes most change during manufacture, and that the other substances are not appreciably altered in amount.

Nanninga (*Korte Berichten uit S'Land Plantentuin*, 1901, 12 and *Technologie du Thé*, 1926, pp. 141-164), studied the transformations undergone by the leaf constituents by extracting the leaf with different organic solvents as well as water. The solvents used were chloroform, ether, acetic ether, alcohol and water, but although this work is of great interest, it is too academic in character to give a proper account of it in an article of this nature. Suffice it to say that Nanninga came to the following conclusions which are in agreement with those of other workers:—

(1) The same kind of changes occur during the fermentation of Java or Assam teas.

(2) The longer the fermentation the greater the decrease in free tannin.

(3) The longer the fermentation the more insoluble products are formed, and a knowledge of these changes affords a possible chemical criterion of when to stop the fermentation.

Bamber also found a decrease in the tannin content of the leaf during manufacture (*Proc. Planters' Association of Ceylon*, 1900, 94.) and states that as a result of several experiments and analyses it was found that the same changes were obtained in every case.

Mann (*The Fermentation of Tea*, 1906, Pt. I; 1907, Pt.II) studied the effect of fermentation on the water soluble material of the leaf and came to the conclusion that the soluble matter including the tannin decreases immediately fermentation sets in, and that at first the decrease is proportional to the period of fermentation.

Fermentation is thus accompanied by a loss of soluble material in the leaf, and this loss is mainly due to a loss of tannin bodies. The decrease in soluble material proceeds rapidly as soon as the leaf is crushed in the rolling, but the rate at which it goes on diminishes in time so that after 5-5½ hours there is very little change observed.

However, along with the decrease in the soluble material, fermentation also results in the production of red coloured liquors, and a probable explanation of this phenomenon has been given by Deuss (*Meded. v.h. Proefstation v. Thee*, 1913, 27) who studied the chemistry of tannin separated from the tea leaf. Nanninga (*Meded. uit S'Land Plantentuin*, 1901, 46.) had already isolated tannin from the tea leaf and described it as a crystalline powder, which is strongly hygroscopic and is rapidly changed to a brown syrupy mass on exposure to the air. Deuss used a different method for purifying the tannin but failed to obtain a crystalline product. He was able to precipitate the tannin from solution in the form of white flakes which could be dried off to a white powder for analysis and characterisation. This compound had a molecular weight of 740, and the molecule contained eight phenolic groups but no carboxyl groups. It reduced ammoniacal silver solutions and Fehling's solution, and gave a yellow precipitate with phenyl hydrazine. Deuss points out that these reactions indicate the presence of ketone groups in the molecule and that these are probably important groupings when the changes which tannin undergoes during fermentation are considered. Ordinary tannin contains only six phenolic groups, so that the tannin isolated by Deuss from tea is different from ordinary tannin. Tea tannin was found to be exceedingly unstable in the presence of impurities or small quantities of water, and it readily forms red derivatives called phlobaphenes. On account of this property Deuss classifies tea tannin with the group of oak tannin which also gives red derivatives on treatment with acid. These red products are soluble in an aqueous solution of tannin, and it is suggested that the coppery colour of made tea is due to the formation of these compounds and their subsequent solution in the tannin liquors of tea. If the oxidation is allowed to proceed too far then brown oxidation products are formed and the liquors are dull. Whether red or brown oxidation products are formed seems to depend in some way on the humidity of the air surrounding the leaf.

I have followed some of the changes which take place in the fermenting leaf, and the results obtained are in agreement with those of the other workers. It will be seen from Table I. how the constituents of the leaf vary in amount during the process of manufacture.

TABLE I.

Changes in the composition of the tea leaf during rolling and fermentation.

Leaf Material	Percentages.				
	Extract.	Total Tannin.	Acid-soluble tannin.	Non-tannin substances.	Nitrogen in extract.
Withered leaf	41·7	17·0	16·0	24·7	1·65
Leaf rolled 15 mins.	40·5	16·7	15·4	23·8	1·62
Leaf rolled 30 ,,	39·4	16·0	14·5	23·0	1·62
Dhool fermented 30 mins	38·6	15·0	12·6	23·6	1·67
,, ,, 60 ,,	38·1	14·6	12·0	23·5	1·66
,, ,, 90	37·3	14·1	11·3	23·2	1·67
,, ,, 120 ,,	37·2	13·9	11·2	23·3	1·65

The water-soluble material of the leaf as depicted by the extract decreases as soon as the leaf is rolled and the fermentation started as a result of gently crushing the leaves. The tannin content follows the extract, but the loss of tannin does not represent the total loss of soluble material since there is a slight decrease in the non-tannin fraction of the extract. More than 50 per cent. of the decrease observed in these substances appears to take place during the first roll. In spite of this the decrease in the extract may be taken as a fairly good guide of the decrease in the tannin fraction. The weight of extract rendered insoluble between each determination was 1.2, 1.1, 0.8, 0.5, 0.8, 0.1, and the loss in tannin between the same periods was 0.3, 0.7, 1.0, 0.4, 0.5, 0.2. These figures show that the process which renders the tannin insoluble slows up after a time so that the observed change is very slow after a few hours. Further, when the rate of decrease in soluble material is compared with the rate at which the fermenting leaf takes up oxygen (Fig. 1) it will be seen that the two curves follow each other very closely, and this fact supports the contention that the decrease in soluble extract observed during fermentation is connected in some way with the absorption of oxygen from the atmosphere. Since most of this loss is due to the disappearance of the tannin in the leaf, it is fair to assume that one of the processes in tea fermentation is the oxidation of tannin.

The change in the tannin from a soluble to an insoluble compound, however, is not the only transformation observed, as it is well known that the colour of the liquors becomes redder. Accoring to Deuss this is due to the formation of tannin red which then dissolves in the tannin solution obtained when the tea is infused with water. At the same time there is formed a water-soluble substance which is precipitated on acidifying the solution. This substance is not present in the liquor obtained from fresh or withered leaf, but

when the liquors of rolled or fermented leaf are acidified it is immediately precipitated as a brownish, flocculent precipitate, leaving a perfectly clear but coloured supernatant liquor. This precipitable substance is formed in increasing quantities as the leaf is allowed to ferment, and in the experiment which gave the results shown in Table I., it increased as follows:—1.0, 1.3, 1.5, 2.4, 2.6, 2.8, 2.7. In the experiment under consideration withered leaf is shown as containing a small quantity of this material but its presence is due to the fact that it is very difficult to avoid some fermentation in withering leaf under practical conditions. When the leaf is carefully withered a precipitate is not obtained on acidifying the liquor obtained from such leaf. This product is therefore formed as a result of fermentation and a similar product can be obtained by oxidising the tea tannin in an extract of fresh leaf with iodine or permanganate and then acidfying with hydrochloric acid. In this way a flocculent precipitate is obtained as a result of the oxidation of the tannin, but it is not known as yet whether this precipitate is the same as that obtained on acidifying an extract of made tea. It is clear, however, that insoluble substances are formed when tea tannin is oxidised, and that substances of this nature are formed during the fermentation of tea, which is a further support of the contention that one process taking place during tea manufacture is that of the oxidation of the tannin complex.

Although we can follow some of the changes which the tannin complex undergoes during tea fermentation, there are other subtle transformations which are not always easy to assess. A tea extract contains a good deal of colloidal material which is liable to undergo change in its physical nature as a result of temperature and moisture conditions, and, although the chemical change involved may be very small, the effect on the physical properties of the solution is considerable. Some at least of the tannin complex of tea exists in this form and its state of aggregation appears to be changed during the process of tea manufacture, but nothing appears to be known concerning the colloidal properties of a tea extract although this promises to be a fertile field for investigation.

Finally, it will be observed that the nitrogen extracted by hot water remains very constant in all the extracts and it is thus concluded that the nitrogenous compounds do not play a very important part in tea fermentation.

(*To be continued*)