ON THE CHEMICAL BASIS OF QUALITY IN BLACK TEA

G. W. Sanderson

The flavour and the aroma of foods are due to the peculiar stimulation of sensory cells located in the human palate and nose by certain chemical compounds contained in the food ; hence we say that there is a chemical basis for all flavours and aromas. Because quality in black tea is a characteristic taste (and possibly also a characteristic aroma) of the tea liquor, there must be a chemical basis of quality in black tea. Further, because black tea quality appears during the fermentation stage of tea manufacture, it is concluded that some, if not all, of the chemical changes occurring during fermentation are instrumental in producing the chemical quantities which constitute quality. A survey of the published work reveals that very little is actually known about the chemical basis of quality in black tea at the present time. It is charged that this is probably so because of a preoccupation with the changes undergone by the flavanols (catechins) during fermentation, which is an almost universal feature of previous investigations. Recent investigations have shown, however, that several different chemical changes take place during fermentation which are likely to be important for the production of quality. A new scheme for tea fermentation is proposed in which an attempt is made to show how flavanol oxidation (catalyzed by catechol oxidase) can bring about the other chemical changes which are here suggested to be of primary importance in the production of quality. It must be said that an accurate description of the chemical basis of quality in black tea must await the results of additional research.

Introduction

It is generally realized that the flavour and aroma of tea (or any food) are due to its chemical composition. The human palate and nose have sensory cells on their surfaces which, when stimulated by the chemical substances to which they are sensitive, cause a message to be transmitted to the brain causing the person to taste and to smell (Pfaffman 1964). Individual chemical compounds often have easily recognized tastes and smells (familiar examples are sugar, salt and vanillin) but the flavour and aroma of food products are generally due to a complex mixture of chemical compounds present in the food product—and tea is no exception.

A particular food would be said to have quality or flavour when the chemical compounds which go to make up its taste and aroma are present in such proportions as to have the desired effect on the palate and nose. With this background we will make the following definitions: *Quality* in tea is a distinct and desirable effect on the palate and nose and the *chemical basis of quality* in black tea is the chemical compounds and their levels in the liquors of the black tea which produce this effect. It should be noted that quality is an independent recognizable characteristic of black tea. That is to say, quality *per se* is not to be confused with colour, strength, or any other real characteristic of black tea, nor is quality necessarily associated with any other real characteristic of black tea.

The task of the tea chemist in elucidating the chemical basis of quality can now be clearly seen. He must identify the chemical compounds present in tea which contribute to its taste and aroma (quality), and he must determine, in both an absolute and a relative sense, the levels of these compounds which are necessary to produce quality.

What is known of the chemical basis of quality?

The late Dr E. A. H. Roberts who worked for the Indian Tea Association until his death in 1962, was a very industrious and productive investigator who sought after the chemical basis of quality in tea for over 20 years. Roberts' last published paper (Roberts 1962a) makes it quite clear that he placed a great deal of importance on the theaflavins and thearubigins as factors determining the liquoring characteristics of black tea. These substances are both oxidation products of the flavanols (also called catechins and polyphenols) and their level in black tea is usually found to be correlated with colour and strength and frequently they are found to correlate with quality. However, Dr Roberts also noted that many cases can be found where there is no correlation between the levels of theaflavins, thearubigins, and quality, and this observation lead him to state that the flavanols and their oxidation products were not the only factors determining quality. In an article on the "Assessment of Quality in Teas by Chemical Means", Roberts (1962b) writes, "Chemical analysis is not sufficient to assess market value of a sample of tea, but it is, even at the present stage, very suitable for comparing teas in manufacture and for choosing conditions to give the best liquor in terms of all characteristics *except* odour and *quality*". This statement speaks for itself. Roberts' ideas on the chemical basis of the several tea characteristics are summarized in Table 1.

TABLE 1—*The chemical basis of "quality" given by Roberts (1962b)*

Name of liquor characteristic (component of quality*)	Chemical basis of the characteristic	Method of measuring
Aroma	Unknown volatile compounds	Smell
Colour, brightness	Theaflavins	Visual or chemical
Colour, total depth	Thearubigins	Visual or chemical
Strength	Thearubigins	Taste or chemical
Briskness	Theaflavins plus caffeine	Taste or chemical
Quality	Theaflavins (?) plus unknown volatile compounds	Taste

**It should be noted that Roberts uses quality in two different senses at the same time. That is, he uses the term quality as a summation of* all *the good points in a tea and at the same time he uses it to denote a specific characteristic of tea.*

A broader though less intensive investigation was carried out by Mr M. S. Ramaswamy at the Tea Research Institute of Ceylon. A summary of Ramaswamy's findings is shown in Table 2 (extracted from Ramaswamy 1963). In the investigation summarized here, samples of made tea from 8 estates in Ceylon were collected once a month over a period of 13 months. The samples were analysed chemically and they were evaluated by tea tasters in Colombo. As can be seen from Table 2, highly significant correlations were found to exist between the tasters' evaluations for quality and the levels of mineral constituents (ash), total oxidizable substances, acid soluble oxidizable substances and theaflavins. It is interesting to note that all of these chemical quantities with the exception of the mineral constituents are composed almost entirely of the flavanols and their oxidation products.

TABLE 2—*Relationship reported by Ramaswamy (1963) between certain chemical quantities in black tea liquors and tea tasters' valuations for quality*

Chemical quantity	Number of tasters whose valuation showed significance correlation ($P<0.05$)	Nature of correlation
Total soluble solids	5 of 8	Positive
Mineral constituents (ash)	8 of 8	Negative
Total oxidizable substances	7 of 8	Positive
Acid soluble oxidizable substances	8 of 8	Positive
Free volatile organic substances	4 of 8	Positive
Hydrolyzable volatile organic substances	None	—
Absorption of light	None	—
Theaflavins	8 of 8	Positive
Caffeine	3 of 8	Negative
Nitrogen other than caffeine nitrogen	5 of 8	Negative

Dr R. L. Wickremasinghe of the Tea Research Institute of Ceylon recently reported some studies on the quality of tea which were carried out in England with the collaboration of Dr T. Swain (Wickremasinghe & Swain 1965; Wickremasinghe 1965). Their findings are briefly summarized in Table 3. These results appear to

TABLE 3—*Relationship between certain chemical quantities in tea liquors and flavour in black tea reported by Wickremasinghe and Swain (1965)*

Chemical quantity	Relative level in flavoury and non-flavoury black tea
Amino acids	
Leucine	Flavoury tea less than non-flavoury tea
iso-Leucine	Flavoury tea less than non-flavoury tea
Free ammonia (NH_3)	Flavoury tea less than non-flavoury tea
Methylbutraldehydes	Flavoury tea less than non-flavoury tea

Relationship between the above chemical quantities can be diagrammatically shown as follows :

$$\text{Leucine} \xrightarrow{\text{(oxidation)}} \text{3-methylbutraldehyde} + CO_2 + NH_3$$

$$\text{iso-Leucine} \xrightarrow{\text{(oxidation)}} \text{2-methylbutraldehyde} + CO_2 + NH_3$$

point out the importance of amino acids in determining tea quality. These workers found that flavoury teas contained lower levels of the amino acids leucine and iso-leucine and lower levels of their oxidation products, methylbutraldehydes and ammonia, than non-flavoury teas. As shown in Table 3, these chemical quantities are all related and, therefore, the results may be simply interpreted to indicate that high levels of the amino acids leucine and iso-leucine are detrimental to the development of flavour. Other results reported by these investigators relating to the theaflavin and thearubigin content of the black teas studied, point out the lack of correlation often found between these chemical quantities and quality in black tea.

Recently Roberts & Sanderson (1965) have found that there is a negative relationship between the total free amino acid content of flush and the quality classification of the clone from which it came. These findings appear to support those of Wickremasinghe & Swain (1965) and they suggest that free amino acids somehow impair the development of flavour and quality. The mechanism for this can only be speculated on at present.

The brief discussion of our knowledge concerning the chemical basis of quality in tea highlights how little we really know about this subject at the present time. Evidence now accumulating suggests that the lack of success in former investigations was due to a general preoccupation with the polyphenols found in tea. This is perhaps natural since the polyphenols are so abundant in tea that the other constituents almost appear to be insignificant in contrast. This is shown in Table 4.

TABLE 4—*General analysis of tea (Adapted from a table given by Vuataz, Brandenberger and Egli 1959)*

Chemical quantity	Content in fresh flush (% of dry weight)	Content in made tea* (% of total dry matter in tea liquor
Proteins	15.2	0
Fiber	30.3	0
Pigments	5.6	0
Caffeine	4.6	9.8
Polyphenols	31.9	68.4
Amino acids	4.2	9.0
Ash	4.4	4.7
Carbohydrates	3.8	8.1

**These chemical quantities would have been altered to a greater or lesser extent during the manufacturing process and they would not necessarily be recognizable as the quantity in the fresh flush from which they were derived.*

where the chemical composition of a representative sample of flush is given. Examination of this table reveals the preponderance of the polyphenols in this plant material which becomes even greater in the liquor of the made tea. However, the paucity of information available on the chemical basis of quality in black tea after all the effort which has been expended on this problem strongly suggests the inadequacy of the approach to the problem taken in the past. Recent investigations on changes undergone by the tea polyphenols during fermentation have lead Bhatia and Ullah (1965) to a similar conclusion.

The source of quality in black tea and the importance of fermentation in developing this quality

Before going on to consider the chemical basis of quality in black tea further, it is important to consider the source of this quality. This question has two important aspects, namely the chemical composition of the starting material (fresh flush) and the changes it undergoes during the manufacturing process (Figure 1 in Sanderson and Kanapathipillai 1964).

The importance of the chemical composition of the flush in making quality tea has been stressed before (Sanderson 1964a) and it suffices here to emphasize two points. First, the black tea of commerce is made from the tea plant (*Camellia sinensis* L.) and not from other plants because of its peculiar chemical composition. Second, some clones of tea are capable of being made into high quality black tea while others are not (Keegel 1959 ; 1962), and this is in large part, due to genetical differences which cause differences in their chemical composition (Sanderson 1964a).

The second aspect of the source of quality in tea has to do with the chemical changes which take place in the flush during tea manufacture. The chemical changes known to occur during withering have been discussed in detail recently (Sanderson 1964b). There is little doubt that they have an important effect on the amount of quality which can be realised from a given batch of tea, but it is the fermentation step in which the quality of black tea is actually developed. The importance of fermentation in tea manufacture in the development of quality in tea may be inferred from the fact that infusions of fresh flush or of green tea do not have black tea quality. Therefore, the elements of black tea quality are produced entirely, or at least in part, during fermentation. If this is true, and it most probably is, then a look at the chemical changes occurring during fermentation should be most instructive in helping us to identify the chemical basis of this quality.

Old schemes for fermentation

Without exception, schemes for fermentation which have been presented previously have dealt entirely with the transformations undergone by the flavanols (catechins). This is exemplified by the scheme put forth almost twenty years ago by Dr A. E. Bradfield (Bradfield 1946). This scheme, shown in Figure 1, has

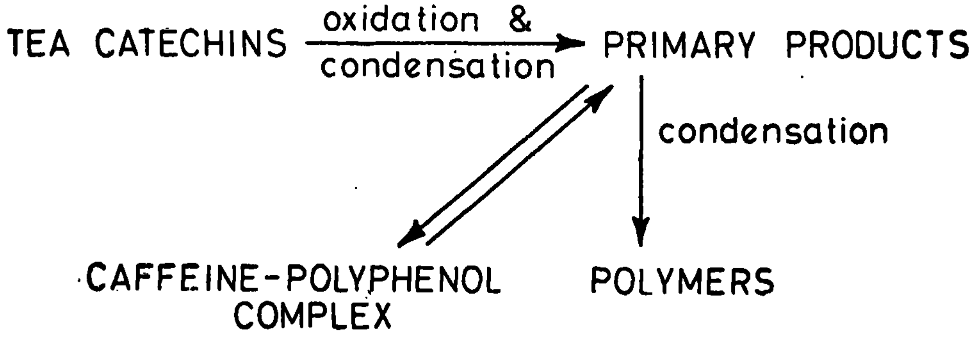

FIGURE 1 — *Scheme (provisional) for tea fermentation proposed by Dr A. E. Bradfield (1946)*

been reproduced virtually unchanged by several authors (Lamb 1958; Eden 1958; Ramaswamy 1958), and in many ways the most recent schemes to be proposed (Roberts 1958; 1962), shown in Figure 2, are only detailed expansions of Bradfield's scheme which incorporate more recent information on the reactions undergone by the flavanols. (These later schemes serve as the basis for recent discussions of fermentation by Stahl 1962; Harler 1963; and Bhatia 1963.) New evidence, however indicates that these 'old' schemes are not complete and that the omissions may be the most important part of fermentation when one is considering quality.

Evidence for changes in chemical quantities other than polyphenols during fermentation

Recently, several investigations have been carried out which clearly show that many changes take place during fermentation in addition to those being undergone by the polyphenols. The most thoroughly studied of these 'extra-polyphenol' changes are those undergone by the amino acids. It was reported some years ago by Russian workers (Bokuchava & Popov 1954) that amino acids could give rise to volatile compounds having pleasant aromas when added to solutions of flavanols undergoing oxidation (fermentation). It has now been shown that amino acids present in fresh flush and to an even greater extent in withered flush (Roberts and Wood 1951; Roberts and Sanderson 1965), are reduced in amount during the fermentation process (Wickremasinghe and Swain 1965; Roberts and Sanderson 1965). Furthermore, Wickremasinghe and Swain (1964; 1965) have shown that there is an increase in certain volatile aldehydes concomitant with a decrease in the level of the related amino acids (Table 2). All these results suggest that amino acids are involved in the formation of chemical quantities during fermentation which determine quality in the black tea.

In another investigation (Roberts and Sanderson 1965) it was shown that there tends to be an inverse relationship between the level of free amino acids at the end of the withering period and the quality of the teas produced. On the other hand, colour appears to be directly related to free amino acid levels (Sanderson 1964b).

Our investigations have shown that during fermentation there is a decrease in soluble carbohydrates (Sanderson and Perera 1965), changes in the level of some organic acids (Sanderson & Selvendran 1965), a decrease in α-keto acids (Wickremasinghe 1965b) and a decrease in the level of some carotenoid compounds (Tirimanna and Wickremasinghe 1965). Undoubtedly, there are many more changes taking place which still await discovery. Very little is known as yet about the fate of the several chemical quantities which diminish during fermentation, but it would be a conservative statement to say that it is likely that some are involved in the development of quality.

Proposal of a new scheme for fermentation

Consideration of the evidence discussed above and elsewhere (Sanderson 1965a) has lead to the development of a new scheme for fermentation which is outlined in Figure 3. The salient points of this scheme may be outlined as follows: The enzyme catechol oxidase and its substrates, the flavanols, are brought into contact with one another in the rolling process and fermentation begins (Sanderson 1965b). The action of catechol oxidase on the flavanols (in the presence of oxygen) causes the flavanols to become oxidized. The oxidized flavanols are themselves very powerful oxidizing agents which are known to be able to oxidize other compounds non-enzymatically (Bokuchava and Popov 1954; Roberts 1957; 1959; Wickremasinghe and Swain 1964). It is proposed in this new scheme for black tea fermentation

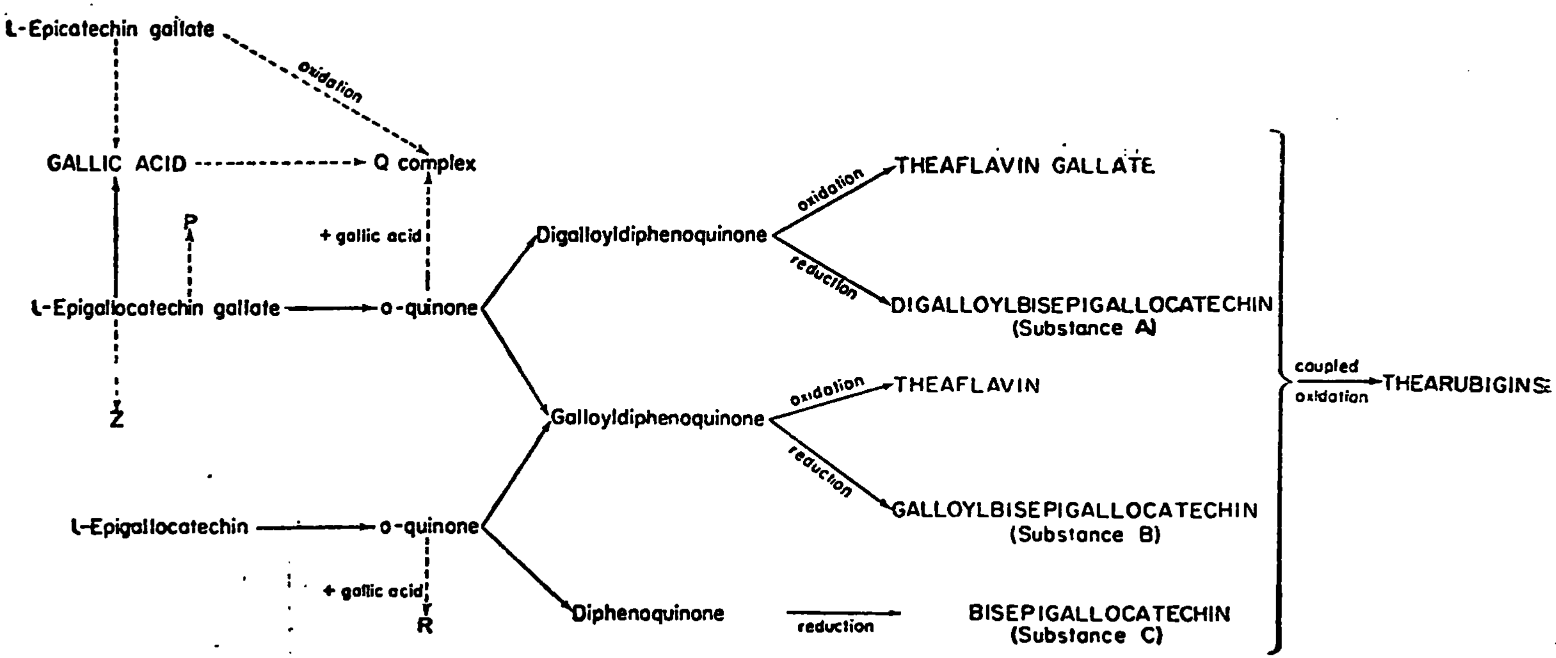

FIGURE 2 — *Scheme for tea fermentation proposed by Dr E. A. H. Roberts (1962a)*

that the oxidized flavanols do in fact cause many chemical quantities present in the fermenting tea flush to become oxidized and in the process of oxidizing other compounds they are reduced back to their original state; a cyclic process. Furthermore, it is proposed that the compounds which comprise quality, and which are formed in fermentation, are formed as a result of flavanol oxidation but the flavanols themselves are not a major part of quality *per se*. The flavanols are shown to have a cyclic role in the formation of quality. The cyclic action of the flavanols, however, can be broken by the joining of two oxidized flavanol molecules (called dimerization) to form the golden brown coloured theaflavins. It is believed that the theaflavins can be further inactivated by oxidation and condensation with amino acids to form the dark brown and insoluble thearubigins.

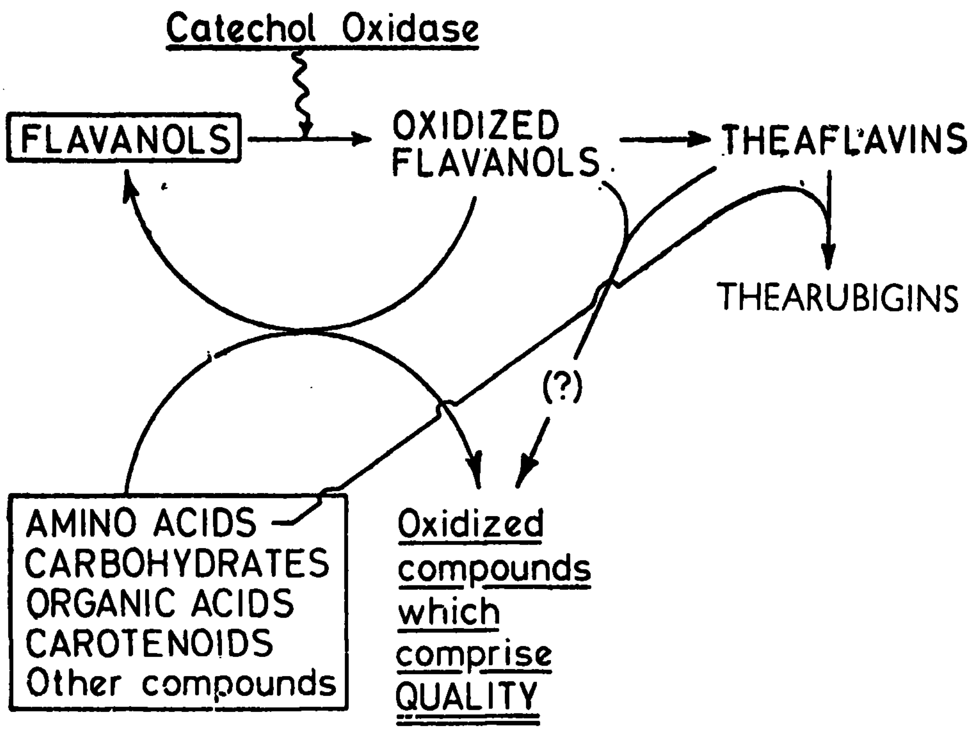

FIGURE 3 — *A proposed new scheme for tea fermentation*

An important feature of this scheme is that it offers an explanation for the interrelationship between colour and quality formation. Both colour and quality formation are dependent on the same reaction, namely the catechol oxidase-catalyzed oxidation of the flavanols. If the coloured theaflavins and thearubigins are formed at too fast a rate there will be little cycling of flavanols with the result that little quality will be formed. The role of amino acids in colour formation is very imperfectly known but the information available at present appears to fit into the scheme as shown in Figure 3. That is, the amino acids may be oxidized to volatile compounds during fermentation which would contribute to quality. However, the amino acids may also interact with the oxidized flavanols to form dark coloured substances (thearubigins?) and this could lead to a reduction in amount of quality which is formed by preventing flavanol cycling.

It was mentioned in a preceding section that the chemical composition of the fresh flush was important to the production of quality in black tea. This is illustrated in the outline of the proposed scheme of fermentation given in Figure 3 where the chemical quantities present in the fresh (withered) flush are enclosed in rectangles. It is easy to see that without the requisite starting materials it is impossible to produce quality no matter how good the other conditions for fermentation are. It is believed that quality potential of clones can be traced back to their genetically controlled chemical composition (Sanderson 1964a), and that at least part of the effect of climate on quality is due to its effect on the chemical composition of the flush (Sanderson 1964a; Sanderson & Kanapathipillai 1964).

The scheme for fermentation proposed here, and outlined in Figure 3, is admittedly highly speculative, but at the same time it appears to explain much of the information on record to date. The ideas incorporated into this scheme needs to be amenable to experimental verification and it is hoped that the necessary investigations will be carried out in the near future. Whatever the result of these new investigations, the ideas put forth here should help to stimulate the research and the development of the new ideas required for further elucidation of the chemical basis of quality in black tea.

Summary and conclusions

The above discussion can be very briefly summarized as follows:

1 – There is a chemical basis to quality in black tea.

2 – Black tea quality is formed during the fermentation stage of tea manufacture through chemical transformation of chemical quantities which *must* be present in fresh (withered) flush.

3 – The chemical basis of quality is only poorly known at the present time but the available evidence suggests that it is very complex and that it involves several chemical quantities other than the flavanols.

4 – A new scheme for fermentation is proposed to explain our present knowledge of the mechanism of the formation of quality in black tea.

What are the practical implications of all this discussion? It is to be expected that eventually it will be possible to maintain fields of tea so as to have the maximum possible quality potential in the flush at all times and then to be able to determine manufacturing conditions which will ensure the full realization of this potential. However, for the moment, it must suffice to say that cultural and manufacturing conditions *do* have an effect on quality and, therefore, it is important to carry out *all* operations involved in the production of tea according to the best procedures known.

References

BHATIA, I. S. (1963). Chemical aspects of green leaf processing. *Two & a Bud* **10** (2) : 28-36.

BHATIA, I. S. & ULLAH, M. R. (1965). Quantitative changes in the polyphenols during the processing of tea leaf and their relation to liquor characters of made tea. *J. Sci. Fd Agric.* **16** : 408-416.

BOKUCHAVA, M. A. & POPOV, V. R. (1954). The significance of amino acids in the formation of tea aroma by interactions with tannin substances under conditions of elevated temperature. *Dokl. Akad. NAUK. SSSR*, **99** : 145-148 ; cited in *Chem. Abstr.* **49** : 3439.

BRADFIELD, A. E. (1946). Some recent developments with chemistry of tea. *Chem. and Ind.* : 242-244.

EDEN, T. (1956). '*Tea*'. 201 pp. London: Longmans, Green & Co.

HARLER, C. R. (1963. '*Tea Manufacture*'. 126 pp. Oxford: University Press.

KEEGEL, E. L. (1959). Tea made from clones. *Tea Quart.* **30:** 134-141.

KEEGEL, E. L. (1962). Tea made from clones II. *Tea Quart.* **33:** 183-188.

LAMB, J. (1958). The Principles of tea manufacture, Chapter I in KEEGEL, E. L. (1958) '*Tea Manufacture in Ceylon*'. 179 pp. Talawakele, Tea Research Institute of Ceylon.

PFAFFMAN, C. (1964). Taste, its sensory and motivating properties. *Amer. Scient.* **52:** 187-206.

RAMASWAMY, M. S. (1958). The chemistry of tea manufacture. *Tea Quart.* **29:** 95-98.

RAMASWAMY, M. S. (1963). Chemical basis of liquoring characteristics of Ceylon tea. 2. Relationship between composition of the tea liquors and the valuations for the liquoring characteristics of black tea. *Tea Quart.* **34:** 56-67.

ROBERTS, E. A. H. (1957). Oxidation-reduction potentials in tea fermentation. *Chem. & Ind.* 1354-1355.

ROBERTS, E. A. H. (1958). The chemistry of tea manufacture. *J. Sci. Fd Agric.* **9:** 381-390.

ROBERTS, E. A. H. (1959). The interaction of flavanol orthoquinones with cysteine and glutathione. *Chem. & Ind.* 995.

ROBERTS, E. A. H. (1962a). Economic importance of flavonoid substances: Tea fermentation. In '*The Chemistry of Flavonoid Compounds*'. 666 pp. ed. T. A. Geissman, p. 468-512. London: Pergamon Press.

ROBERTS, E. A. H. (1962b). Assessment of quality in teas by chemical means. *Two & a Bud* **9** (3): 3-8.

ROBERTS, G. R. & SANDERSON, G. W. (1965). A study of the changes undergone by free amino acids during the manufacture of black tea. *J. Sci. Fd Agric.* (In the press).

SANDERSON, G. W. (1964a). The chemical composition of fresh tea flush as affected by clone and climate. *Tea Quart.* **35:** 101-110.

SANDERSON, G. W. (1964b). The theory of withering in tea manufacture. *Tea Quart.* **35:** 146-163.

SANDERSON, G. W. (1965a). The action of polyphenolic compounds on enzymes. *Biochem. J.* **95:** 24-25 p.

SANDERSON, G. W. (1965b). On the nature of the enzyme catechol oxidase in tea plants. *Tea Quart.* **36:** 103-111.

SANDERSON, G. W. & KANAPATHIPILLAI, P. (1964). Further studies on the affect of climate on the chemical composition of fresh tea flush. *Tea Quart.* **35:** 222-229.

SANDERSON, G. W. & PERERA, B. P. M. (1965). Carbohydrates in tea plants. 1. The carbohydrates of tea shoot tips. *Tea Quart.* **36**: 6-13.

SANDERSON, G. W. & SELVENDRAN, R. R. (1965). The organic acids in tea plants A study of the non- volatile organic acids separated on silica gel. *J. Sci. Fd Agric.* **16:** 251-258.

STAHL, W. H. (1962). The chemistry of tea and tea manufacturing. *Advance. Fd Res.* **11:** 201-262.

TIRIMANNA, A. S. L. & WICKREMASINGHE, R. L. (1965). Studies on the quality and flavour of tea—2—The carotenoids. *Tea Quart.* **36:** 115-121.

VUATAZ, L., BRANDENBERGER, H. & EGLI, R. H. (1959). Plant Phenols. 1. Separation of the tea leaf polyphenols by cellulose column chromatography. *J. Chromatog.* **2:** 173-187.

WICKREMASINGHE, R. L. (1965a). Studies on the quality and flavour of tea. 1—The polyphenols and low-boiling volatile compounds. *Tea Quart.* **36:** 59-63.

WICKREMASINGHE, R. L. (1965b). Report of the Biochemist (Manufacture) for 1964. *Rep. Tea Res. Inst. Ceylon* 1964 **2:** 106-107.

WICKREMASINGHE, R. L. & SWAIN, T. (1964). The flavour of black tea. *Chem. & Ind.* 1574-1575.

WICKREMASINGHE, R. L. & SWAIN, T. (1965). Studies of the quality and flavour of Ceylon tea. *J. Sci. Fd Agric.* **16:** 57-64.