

# STUDIES ON THE QUALITY AND FLAVOUR OF TEA

## I—THE POLYPHENOLS AND LOW-BOILING VOLATILE COMPOUNDS

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The work described in this article is part of an investigation, carried out in Cambridge, of the polyphenols and low-boiling volatile compounds of tea. This study was made during my tenure of a Fellowship awarded by the TRI, and a more detailed account of the findings has been published elsewhere, (Wickremasinghe and Swain 1965).

Among the products of fermentation of tea leaf, Roberts and Myers (1959), isolated theaflavin and theaflavin gallate, as well as a group of compounds, referred to as thearubigins. The amounts of these were shown to determine strength and colour of liquors, and to play an important part in the assessment of quality (Roberts and Smith 1961). Quality, however, is also dependent on other factors, including the volatile constituents responsible for the characteristic aroma of tea. Analysis of the essential oil of tea by Japanese workers, (Yamanishi, Kiribuchi, Sakai, Fujita, Ikada and Sasa 1963), showed the presence of at least 27 components and to these must be added the volatile fatty acids identified by Brandenberger and Muller (1962). Not all of the volatile compounds of tea however, exist as such in black tea—many of them are formed during brewing by the interaction of non-volatile compounds. Bokuchava and Popov, (1954), showed that the addition of different amino-acids to hot aqueous infusions of tea led to the production of different aromas, and that no aroma developed if an aldehyde-binding reagent was added. More recently, Wickremasinghe and Swain (1964), have shown that both glucose and oxidised catechin react with the amino-acids, leucine and valine, to produce the aldehydes expected to arise from these amino-acids.

### Material

The two fresh tea leaf samples and 8 black tea samples were obtained through the kindness of Dr G. W. Sanderson, who made arrangements for having them flown from Ceylon to London. The fresh tea leaf was refrigerated during transit and received in Cambridge two to three days after plucking, apparently in good condition. However, chemical wither, (Sanderson 1964), of the green leaf would necessarily have occurred during transit and this fact should be borne in mind when assessing the results. The other samples of black tea examined were kindly supplied by Messrs Wm. Jas & Hy. Thompson and Messrs Kerr, Hope & Sons, both of London, who were also good enough to report on the black tea samples.

### Methods

*Preparation of extracts:* Extracts were made first with boiling absolute methanol after which the residue was re-extracted with boiling aqueous methanol.

*Polyphenols:* Polyphenols were identified by paper chromatography and estimated by the methods described by Swain and Hillis (1959) ; theaflavins and thearubigins were measured as described by Roberts and Smith (1961).

*Volatile Compounds:* Volatile compounds were identified and estimated by gas-liquid chromatography.

## Results and Discussion

*Polyphenols*: The polyphenolic compounds described by Roberts (1958), were identified in the green tea leaf. It was found that the quantities of most of the flavanol spots decreased on fermentation and that this decrease was accompanied by the appearance of theaflavins and thearubigins. Chromatograms of black tea were qualitatively similar to those of fermented tea.

Table I shows the results of quantitative estimations of polyphenols extracted by (a) absolute methanol and (b) aqueous methanol, together with the theaflavin contents, valuation, and countries of origin of the tea samples tested.

TABLE I—Total Polyphenols, theaflavins, and valuations of tea samples

Sample No		Total polyphenols		Theaflavin %	Valuation (Sterling)
		Absolute methanol	Aqueous methanol		
<i>Unprocessed</i>					
1	Leaf	68	16		
	Bud & Stalk	79	27		
2	Leaf	130	13		
	Bud & Stalk	218	51		
<i>Fermented</i>					
1	Leaf	22	9		
2	Bud & Stalk	57	17		
<i>Black</i>					
1	} Ceylon	33	30	11.2	5/3
2		53	31	7.9	4/4
3		20	38	9.9	3/11
4		12	38	5.6	3/8
5		26	35	12.4	5/6
6		38	33	9.0	4/8
7		23	32	4.7	3/6
8		15	35	5.6	3/4
9	Assam	23	37	9.0	4/7
10	Dooars	14	38	8.5	3/7
11	Kenya	34	35	10.1	3/8
12	Uganda	37	35	9.0	3/6
13	S. India	24	38	12.4	4/2
14	Malaya	9	35	5.9	3/4
15	Kenya	26	35	11.3	5/1

Values for total polyphenols expressed as mg/g dry weight of tea in terms of epigallocatechin gallate.

It is seen from Table I that :

- (i) the polyphenol content of the unprocessed terminal bud+stalk is higher than that of the two leaves. This is in agreement with the findings of Roberts (1962),

- (ii) fermentation and firing lead to an increase in the *proportion* of polyphenols soluble in aqueous methanol to those extractable by absolute methanol. This is due to the fact that polymeric compounds are more soluble in aqueous methanol than absolute methanol, (*cf.* Goldstein and Swain 1963), and hence this technique of differential extraction provides a means of assessing the degree of oxidation and condensation of polyphenols that occurs during manufacture,
- (iii) there is a correlation between theaflavin content and valuation, as has already been reported by Roberts and Smith (1961),
- (iv) the relationship between total polyphenols extracted by *absolute* methanol on the one hand and theaflavin content, (and valuation), on the other, is expressed by a relatively smooth curve (Figure 1). Black teas containing 25-30 mg per g dry weight of polyphenols extracted by absolute methanol were the preferred teas, whilst those containing either more or less than this level contained less theaflavin, and were valued lower. This finding suggests that there is an optimal level of polyphenols in green tea leaf for maximal theaflavin production, since the amount of polyphenols in any black tea would be dependent on the composition of the leaf used in its manufacture,

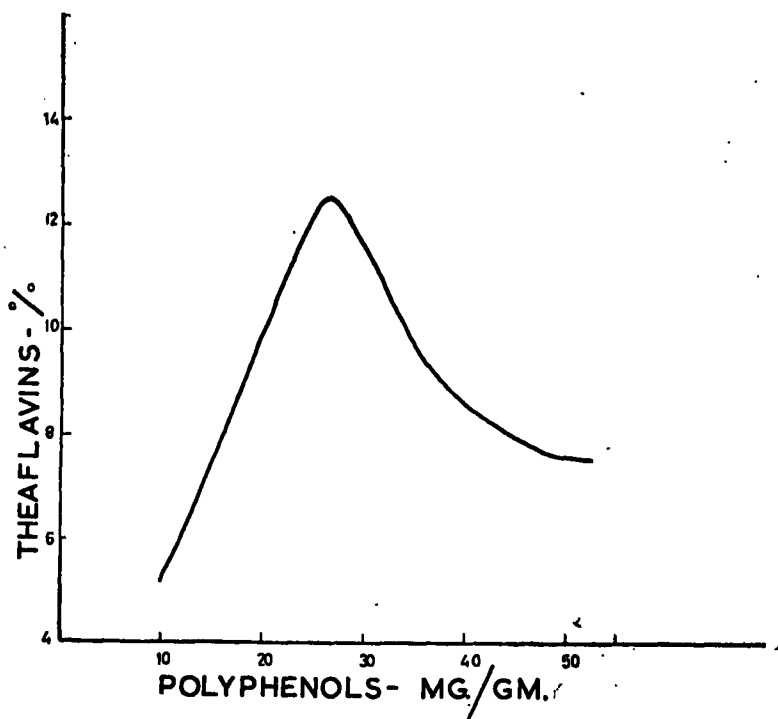


FIGURE 1—*The relationship between total polyphenols extracted by absolute methanol, and Theaflavin content*

- (v) the amounts of total polyphenols extracted by aqueous methanol is relatively constant in all the black tea samples tested. This observation suggests that the oxidation and condensation of polyphenols does not proceed beyond a certain limiting point, *viz* that at which the oxidation products

inactivate enzymic (including polyphenolase) activity. In this connection it has been shown experimentally that oxidation products of catechin inhibit the enzyme tyrosinase, (Wickremasinghe and Swain, unpublished). This hypothesis could explain observation (iv) above in that a low content of polyphenols in the green tea leaf would *per se* limit the theaflavin content in the tea made therefrom, whilst a high concentration would favour the rapid formation of enzyme-inhibiting compounds, which then interfere with the further formation of theaflavin.

#### *Low-boiling Volatile Compounds:*

Quantitative gas liquid chromatography of unprocessed tea leaf showed the presence of hydrogen sulphide, methanethiol, dimethyl sulphide, acetaldehyde, propionaldehyde, isobutyraldehyde and very large amounts of methanol and ethanol. On fermentation the amounts of methanol and ethanol decreased and 1- and 3-methylbutyraldehydes, n-valeraldehyde and diacetyl appeared as additional volatile compounds. In black tea, the amounts of methanol and ethanol were very small and further peaks corresponding to the presence of acrolein, n-butyraldehyde, acetone and methyl ethyl ketone became evident. There was considerable variation in the absolute and relative amounts of the volatiles in the 22 samples of black tea tested and this variation may contribute to the differences in the "bouquets" of the samples. The most striking observation was the wide variation (14 to 159  $\mu$ g/g black tea) of the methylbutyraldehydes in the different samples, and the finding that the concentrations of these aldehydes were generally low in flavoury teas, and high in those without flavour. The possible significance of this finding is, at present being investigated.

The low-boiling volatile compounds identified and estimated here are only part of the aroma complex of tea and much more work is required before the problem of flavour is unravelled. Attempts are now being made to study the higher-boiling volatile compounds and their mode of biogenesis, and the role that these, and other groups of compounds play in determining the quality and flavour of tea.

#### **Summary**

- 1 The polyphenol content of unprocessed terminal bud + stalk is higher than that of the two leaves.
- 2 A simple method is described for assessing the degree of oxidation and condensation of polyphenols during manufacture.
- 3 The relationship between theaflavin content and valuation of black tea samples is confirmed.
- 4 Evidence for the existence of an optimal level of polyphenols in green tea leaf for maximal theaflavin production is discussed.
- 5 Oxidation and condensation of polyphenols during manufacture does not proceed beyond a certain limiting point.
- 6 The results of quantitative studies of the low-boiling volatile compounds of black tea are described.
- 7 The concentrations of methylbutyraldehydes was found to be low in flavoury tea and high in those without flavour.

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