

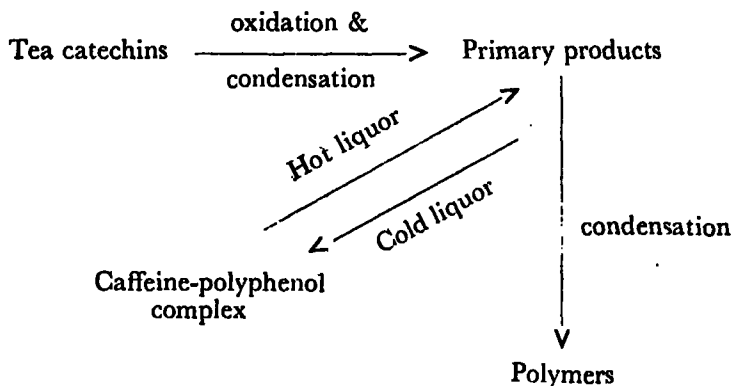
THE CHEMICAL BASIS OF LIQUORING CHARACTERISTICS OF CEYLON TEA

PART I.—FERMENTATION, CONDENSATION AND QUALITY OF THE TEA LIQUORS

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Introduction

Parallel to the investigations being carried out in different research stations on the chemistry of the constituents of the green tea leaf and the biochemical changes occurring to these constituents during the manufacture of tea, research work is also being carried out to discover the nature of the chemical constituents of black tea and their relationship with the liquoring characteristics. Foremost amongst such work are the investigations carried out by Bradfield and his co-workers. It was shown by Bradfield and Penny (1944), that "primarily 'quality' depends not only on the total amount of polyphenols, but also on the proportion present as ethyl-acetate-extractable material" in the tea liquor. Based on the investigations on black tea, Bradfield (1946) suggested the following scheme for the oxidation-condensation of the tea catechins during manufacture and indicated the nature of the constituents responsible for formation of "cream" (caffeine-polyphenol complex) in the tea liquors on cooling:



Bradfield (1948) suggested that the "condensation increases at the expense of the primary products if the wet leaf is fermented or the temperature is higher or the fermentation is prolonged".

After this, Roberts (1957) showed that the ethyl-acetate-extractable material in the tea liquors consisted mostly of theaflavins.

It is reasonable to assume that all workers now accept the view that the primary reaction in tea 'fermentation' is the oxidation of the ortho-dihydroxy groups in tea catechins by the tea polyphenol oxidase and the condensation of the ortho-quinones formed to give rise to the products that are desirable from the point of

view of the consumer of black tea. The green-tea drinker on the other hand prefers the unchanged catechins (for the first stage in the manufacture of green tea is to destroy the oxidase). Whilst the unchanged catechins are soluble both in water and in ethyl acetate, the condensation products have different degrees of solubility in water and ethyl acetate, depending upon their complexity.

The investigations of Bradfield and Penny (1944) were carried out in England with the finished product which had gone through the 'firing' process, (*i.e.* drying with hot air between 120 and 180°F for about 20 minutes) after the completion of the 'fermentation' process. Bradfield (1948) appreciated that during firing "in the short interval of time the leaf juices are heated while evaporation of water is taking place, auto-oxidation, not necessarily following the same course as enzymic oxidation, is conceivable and further condensation may be accelerated . . . these speculations require experimental investigation". It was, therefore, thought desirable to examine further the changes that occur to the water-soluble and ethyl-acetate-soluble constituents during the various stages of manufacture of tea in or near a tea factory.

Material

The green leaf used for all the experiments was obtained from the St Coombs factory bulk supply (elevation, 4,500 ft. AMSL); careful selection of undamaged flush was made from this supply. It should be mentioned that Ceylon tea is very heterogenous and the chemical composition of the leaf varies with different types of leaf. Seasonal variations are also very marked. However, each set of experiments was carried out on leaf from the same batch. Clonal leaf was not available in sufficiently large quantities for this investigation.

Methods

1. DETERMINATION OF THE WATER-SOLUBLE AND THE ETHYL-ACETATE-SOLUBLE CONSTITUENTS

10 g of the made tea or its equivalent of green, withered or fermented leaf was boiled with 250 ml of distilled water for exactly 6 minutes and filtered through a Whatman No. 4 filter paper. When cool, the filtrate was thoroughly stirred and 40 ml aliquots were taken for the various determinations. Relevant corrections were made for the initial moisture content of the test materials.

The water-soluble substances in the extract were determined by evaporation on a water bath in the usual way. For the determination of the ethyl-acetate-extractable substances, the water extract was first treated with chloroform (3 × 100 ml) to remove caffeine and then extracted with ethyl acetate (250 ml) in a Soxhlet liquid extractor for 16 hours.

2. COLORIMETRY

The colour of the various fractions was determined in the Lovibond-Schofield tintometer. The water extract was diluted (1 in 10) to give a concentration which would not 'cream' on cooling. Lovibond colour units are expressed in relation to 100 g dry tea and 250 ml solution using 1 inch cell.

The absorption of light by the extract was determined in an "EEL" photoelectric absorptiometer without a filter. Log scale units are expressed in relation to 100 g dry tea and 250 ml solution using tubes 1 cm in diameter.

3. PERIOD OF FERMENTATION

In all the experiments carried out, the period of fermentation did not include the period taken for rolling or mincing.

Results and Discussion

1. THE WATER-SOLUBLE AND THE ETHYL-ACETATE-EXTRACTABLE SUBSTANCES OF TEA DURING THE VARIOUS STAGES OF ITS MANUFACTURE.

Experiment 1. Green leaf was soft-withered (60% moisture) under laboratory conditions, minced twice, fermented under humid conditions at 70°F for different periods and dried at 205°F.

Experiment 2. The green leaf was hard-withered (48% moisture), passed through the Clivemear roller twice and minced (St Coombs factory conditions). The crushed leaf was brought up to the laboratory and fermented for different periods in a humid atmosphere at 70°F. The fermented leaf was examined without drying it.

The results are shown in Table 1.

TABLE 1.—*The water-soluble and the ethyl-acetate-soluble substances in tea during the various stages of its manufacture*

Expt. No.	Solvent	Soluble substances as % dry tea				
		Green leaf	Withered leaf	Fermented Leaf		
				Fermented for 1.5 hr.	Fermented for 3.5 hr.	
1	Water Ethyl acetate	46	48	38	33	
		19	21	11	8	
2	Water Ethyl acetate	43	50	Fermented for 1 hr.	Fermented for 4 hr.	Fermented for 24 hr.
				47	37	34
				22	13	9

The results suggested that both the water-soluble and the ethyl-acetate-soluble constituents increased slightly during withering and then showed a progressive decrease during fermentation depending upon the period of fermentation. A comparison between the results of Experiment 1 (fired tea) and Experiment 2 (un-fired tea) in Table 1 also suggested that there was a further decrease of these constituents during the firing process.

The increase in the water-soluble and the ethyl-acetate-soluble constituents during withering is probably due to the changes in the leaf constituents other than tea polyphenols. During the subsequent operations, however, the decrease in these constituents are mainly due to the enzymic oxidation of the tea polyphenols and their conversion to theaflavins, and to thearubigins of increasing complexity. The unoxidised polyphenols, the theaflavins, and most of the thearubigins of lower molecular weight are soluble in water while the unoxidised polyphenols, the theaflavins and only part of the thearubigins of lower molecular weight are soluble in ethyl acetate.

In the normal manufacture of tea, under-fermentation gives light yellowish liquor, with a greater amount of soluble substances consisting mostly of unoxidised polyphenols. Normal fermentation gives a bright red liquor consisting of substances which are soluble in water to a lesser extent than the under-fermented leaf. These are mostly theaflavins and to a larger extent thearubigins of lower molecular weight. Part of the highly-condensed dull brown products of oxidation, which are insoluble in water are left in the infused leaf. Over-fermentation gives a dull brownish liquor consisting of a high proportion of the thearubigins to the theaflavins; the water soluble constituents are also reduced; the infused leaf also becomes dark brown in colour probably due to the presence of water-insoluble, condensed products of high complexity. As suggested by Bradfield (1948), 'firing' causes further condensation of these products, and consequently a decreased solubility of these constituents in water and ethyl acetate is found to occur.

2. THE EFFECT OF THE DURATION AND THE TEMPERATURE OF FERMENTATION ON THE VALUATION OF THE TEAS (TASTER'S) AND THE SOLUBILITY OF THE TEA CONSTITUENTS IN WATER AND ETHYL ACETATE.

Withered leaf (St Coombs factory) was rolled in the experimental rollers and sifted to collect the first dhool. Part of the dhool was fermented under normal factory fermenting room conditions while the rest of the dhool was fermented at a higher temperature. The fermented material was then 'fired' under identical conditions in the factory experimental drier. The teas were valued by a Colombo taster. The analytical results together with the valuation of the teas are shown in Table 2.

TABLE 2.—*The effects of the duration and the temperature of fermentation on the tasters' valuation and the solubility of tea constituents in water and ethyl acetate (complete extraction)*

	Temperature of fermentation °F	Period of fermentation hr.	Taster's valuation cents	Soluble substances as % dry tea	
				Water-soluble substances	Ethyl-acetate-extractable substances
Control	68	1.5	190	45	15
	68	2.0	192	43	14
	68	3.0	195	42	14
Experimental	104	1.5	198	42	12
	104	2.0	196	40	11
	104	3.0	192	38	10

The results showed that the substances soluble in water and ethyl acetate decreased as the temperature or the period of fermentation increased. These results are typical of several other experiments carried out. It appears that, under normal manufacturing practice, the water-soluble and the ethyl-acetate-soluble substances fall to a level which bears some relation to the tea taster's opinion of the optimum product; beyond this level, a further fall in solubility corresponds to over-fermentation. The results obtained also support the technological experiments (Keegel 1955) indicating that fermentation could be carried out with advantage at temperatures slightly higher than the normal factory conditions (St Coombs), *provided the period of fermentation is controlled.*

3. EFFECT OF OVER-FERMENTATION OF THE FOURTH DHOOL ON THE VALUATION OF THE TEAS AND THE SUBSTANCES SOLUBLE IN WATER AND ETHYL ACETATE

The material for this experiment was obtained from St Coombs factory. The rolled material from the 4th roll (which had at least partly fermented for nearly 2 hrs. during its passage in the rollers in earlier stages) was fermented for a further period in the factory fermenting room and 'fired' in the factory experimental drier. The results of analysis etc. are shown in Table 3.

TABLE 3.—*Effect of over-fermentation of the fourth dhool on the valuation of the teas and on the substances soluble in water and ethyl acetate*

	Period of fermentation	
	1 hr.	4 hr.
Taster's valuation (cents) ...	205	195
Water-soluble substances (% dry tea) ...	44	42
Ethyl-acetate-extractable substances (% dry tea) ...	13	8

Of particular interest is the loss in the ethyl-acetate-extractable substances and a corresponding loss in the valuation of the over-fermented material.

4. EFFECT OF DIFFERENT TYPES OF ROLLING ON THE VALUATION OF THE TEAS AND THE SUBSTANCES SOLUBLE IN WATER AND ETHYL ACETATE

Tea leaf was subjected to two different types of rolling, but fermentation, etc., were carried out under identical conditions at St Coombs factory. The P.F. tea (pulp-fermented) was made by pulping the green leaf in the Clivemeare roller while the Clivemeare-rolled tea was made by bruising the withered leaf in the Clivemeare roller and then rolling in the normal way in the factory rollers. The results are shown in Table 4.

TABLE 4.—*Effect of different types of rolling on the valuation of the teas and the substances soluble in water and ethyl acetate*

Expt. No.	Type of rolling	Taster's Valuation (cts.)	% dry tea	
			Water-soluble substances	Ethyl-acetate-extractable substances
I	Clivemeare-rolled tea	—	38	14
	Control (normal factory rollers)	—	36	14
II	P.F. tea	185	32	8
	Control (normal factory rollers)	210	31	12

There was practically no difference in the composition of the Clivemeare-rolled tea and that of the tea manufactured by the orthodox methods. On the other hand, the P.F. tea appeared to show a decrease in the ethyl-acetate-extractable substances and a corresponding decrease in its valuation.

5. EFFECT OF DRYING THE FERMENTED LEAF UNDER DIFFERENT CONDITIONS ON THE SOLUBILITY OF MATERIAL IN WATER AND ETHYL ACETATE

In order to assess the possible effect of heat during 'firing' upon the soluble constituents (water and ethyl acetate) fermented leaf from St Coombs factory (1st Dhool, 2.75 hr. fermentation since rolling) was subjected to (a) vacuum drying, (b) preheating for 20 min. at 104°F followed by vacuum drying, (c) prolonged fermentation (6.75 hr. fermentation since rolling) followed by vacuum drying (d) normal factory firing process (control). Vacuum drying will inhibit oxidation through the removal of oxygen. In the early stages of commercial 'firing' which takes 20 min. to complete, the leaf temperature attains about 104°F while still in a moist condition.

The results are shown in Table 5.

TABLE 5.—*Effect of drying the fermented leaf under different conditions on the solubility of material in water and ethyl acetate*

Solvent	Drying conditions			
	(a)	(b)	(c)	(d)
Water ...	43	40	37	40
Ethyl acetate ...	13	11	9	12

It is evident that, as suggested by Bradfield (1948), condensation continues to occur during the 'firing' process. The difference between the vacuum-dried tea (a) and the control (d) was found to be not very marked. This is probably due to the fact that the period taken for commercial 'firing' is very short (about 20 min.) even though it is carried out at high temperatures, while in vacuum, it takes a long time for the leaf to dry. In the latter, the leaf remains in a wet condition for a very long time during which, even though the oxidation process is arrested the condensation process continues to take place.

6. EFFECT OF THE TEMPERATURE AND THE PERIOD OF FERMENTATION ON THE COLOUR OF THE WATER-SOLUBLE AND THE ETHYL-ACETATE-SOLUBLE SUBSTANCES

Green leaf was soft-withered (66% moisture) and minced twice with the finest attachment of the mincing machine. The minced material was then fermented at low (59° ± 2°F), normal (73° ± 2°F) and high (104° ± 4°F) temperatures. The minced leaf was thoroughly stirred up at half-hour intervals. The fermented leaf was drawn at 1 hour and 4 hour intervals for the analysis, without drying it.

The results of the analysis are shown in Table 6.

TABLE 6.—*Effect of the temperature and the period of fermentation on the colour of the water-soluble and ethyl-acetate-soluble substances*

Analysis for	Withered leaf	Fermented Leaf					
		Fermented for 1 hr. at			Fermented for 4 hr. at		
		Low temp.	Normal temp.	High temp.	Low temp.	Normal temp.	High temp.
Water-soluble substances % dry tea	45	40	40	38	38	37	33
Ethyl-acetate-extractable substances % dry tea	25	18	17	15	15	10	7
<i>Colour (Lovibond)</i>							
i. Water-soluble yellow units	—	1317	1619	2090	1951	2095	2150
red units	—	941	952	1091	1074	1047	1032
ii. Ethyl-acetate-soluble yellow units	—	275	298	193	235	203	160
red units	—	250	248	169	209	203	160
<i>Absorption of light (Photo-electric absorptiometer)</i>							
i. Water-soluble	—	1070	1214	1261	1293	1321	1237
ii. Ethyl-acetate soluble	—	695	654	425	418	419	410

The results indicate that parallel to the loss of soluble substances, the total colour of the liquor increases. This increase appears to take place at the expense of the ethyl-acetate-soluble substances.

The results appear to support the hypothesis that the range of intermediate compounds soluble in ethyl acetate increases in complexity as the fermentation proceeds and that brownish polymers, less soluble in ethyl acetate and water, are formed from them. Bradfield (1946) suggested that "without a due proportion of polymerised material, colour and some of the characteristic taste of black tea would be lacking; with too high a proportion, liquor will be cloudy (for these polymers are probably colloiddally dispersed rather than dissolved), brownish, lacking in astringency and will give a poor 'cream' of a brownish shade. With too high a proportion of unchanged catechins, the liquors will lack the characteristics of black tea".

The results indicate the possibilities of radical improvements in the process of tea manufacture. The conservative attitude of the tea trade and to some extent the consumer will however necessitate a very gradual change in the technique of processing, especially because logical improvements are difficult to effect without changing the traditional appearance of the product. The appearance of the black tea is very largely determined by the rolling process which is unnecessarily complicated, but nevertheless highly characteristic in its effect upon the appearance of the final product.

7. THE WATER-SOLUBLE AND ETHYL-ACETATE-EXTRACTABLE SUBSTANCES IN HIGH-GROWN AND LOW-GROWN CEYLON TEAS AND THEIR RELATIONSHIP TO TASTERS' VALUATIONS OF THE TEAS

A number of samples of black tea manufactured in different estates in up-country and low-country districts were obtained (April 1955) with a view to relating

the water-soluble and the ethyl-acetate-extractable constituents to the taster's valuation of the teas.

The results are shown in Table 7.

TABLE 7.—*The water-soluble and ethyl-acetate-extractable constituents in high-grown and low-grown Ceylon teas and their relationship with the taster's valuation of the teas*

(Estates Nos. 1–6 are situated in the up-country region, and estates Nos. 7–12 in the low-country area)

Estate No.	Elevation (ft. AMSL)	The water-soluble substances % dry tea (a)	The ethyl-acetate-extractable substances % dry tea (b)	b/a	Taster's valuation (cts./lb)
1	6200	34.7	12.9	0.372	290
2	4600	34.9	10.7	0.307	240
3	4600	32.7	7.7	0.235	210
4	6100	34.9	9.2	0.264	195
5	5000	36.4	11.0	0.302	190
6	3400	37.3	11.1	0.298	190
7	1100	33.2	8.4	0.253	200
8	1300	37.6	9.9	0.263	195
9	700	34.4	7.5	0.218	195
10	300	35.6	8.3	0.233	190
11	600	35.3	9.4	0.259	185
12	1600	35.1	9.1	0.259	180

These results are typical of several other examinations made and to a large extent comparable with the results obtained by Bradfield and Penny (1944), which are shown in the Table 8 (after recalculation).

TABLE 8.—*The relationship between total and ethyl-acetate-extractable solids from tea liquors (Bradfield and Penny (1944) recalculated)*

Origin of the sample of tea	Total solids % tea (a)	Ethyl-acetate-extractable substances % tea (b)	Ratio b/a
1. Ordinary Sylhet tea (B.P. poor quality)	38.0	8.5	0.224
2. Upper Assam tea (B.O.P. with tips, high quality) ...	42.6	13.2	0.310
3. Ceylon tea (high grown) ...	35.3	9.3	0.263
4. Dooars tea ...	36.5	7.7	0.211
5. Nyasaland tea ...	36.4	7.8	0.214

In comparing the results of Bradfield and Penny for Ceylon high-grown tea (Table 8) with the analytical data for similar teas shown in Table 7, it should be stressed that the results shown in Table 8 appear to cover only a single sample of

each tea; details of the number of samples analysed by Bradfield and Penney (1944) are not mentioned. However, they mention that the tea samples were several years old when they were examined, during which time they had probably undergone some change. The results shown in Table 7, however, refer to freshly manufactured Ceylon teas.

In relating the results of the water-soluble and the ethyl-acetate-extractable substances with the taster's valuation (Table 7), it should be borne in mind that there appears to be fairly wide variations in the manufacturing conditions in different estates; the manufacturing technique also is varied to suit the particular marketing requirements. Further, ultimate practical conclusions depend entirely upon the subjective opinion of the tea tasters. Much work has been done on the standardisation of tasting of experimental samples and on any one occasion, the valuation of experimental teas against a standard is fairly reliable. However, in spite of these difficulties, the results shown in Table 7 indicated that the ratio of the ethyl-acetate-extractable substances to the water-soluble substances was significantly and positively correlated with the taster's valuation ($P < 1\%$). All the same, a valuation could not be given from the chemical data of an isolated case.

Subsequent to the work described in this paper, Roberts (1957) isolated certain constituents which were bright yellow in colour from the ethyl-acetate-extractable fraction of the tea liquors and coined a new term, 'theaflavins', for these constituents; he also showed that the theaflavins were related to the taster's report on liquoring characteristics, particularly with the desirable golden yellow colour of good quality teas. Roberts *et al.* (1959) also mention that "there is some link . . . between the losses in quality and briskness with increasing time of fermentation, and the corresponding fall in the theaflavin content". In Part II of this paper, it will be shown that in Ceylon teas, manufactured by orthodox methods in districts at different elevations and climatic conditions, the theaflavins extracted from the ethyl-acetate-soluble fraction of the tea liquors appeared to show a close relationship with the taster's valuation for the desirable characteristics of a high quality Ceylon tea.

Summary

1. The results of investigations on the water-soluble and the ethyl-acetate-extractable constituents of Ceylon tea during the various stages of its manufacture and under different experimental conditions are reported.

2. There is an increase in the water-soluble and the ethyl-acetate-extractable substances during withering and a gradual decrease of these substances during the subsequent processes of the manufacture of tea.

3. It has been shown that the period and the temperature of fermentation have considerable effect on the solubility of substances in water and in ethyl acetate; parallel to these changes, the colour of the liquors is also affected. Unless the fermentation process is arrested at a stage of intermediate condensation compounds, undesirable polymers are formed. Different types of rolling and conditions of drying also appear to contribute to the changes in the water-soluble and the ethyl-acetate-soluble constituents.

4. There appears to be a positive relationship between the proportion of the ethyl-acetate-extractable substances to the water-soluble substances and the market valuation of the high-grown and low-grown Ceylon teas.

Acknowledgments

I am indebted to Mr J. Lamb, O.B.E. for his kind interest in these investigations. The manufacturing experiments at St Coombs factory were carried out with the kind assistance of Mr S. M. Guneratnam of the Technology Division. I am also grateful to the tasters in Colombo who valued the experimental tea samples.

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