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CHEMICAL CHANGES DURING STORAGE OF BLACK TEA

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Theaflavins, thearubigins, amino acids, polyphenols and moisture contents of tea underwent quantitative changes during storage, and some of these changes were related to the valuation of the stored samples. Theaflavins, as well as catechin levels, contributed to the enhanced valuation of a tea sample.

It is well known that freshly-made black tea has a 'raw' or 'green' taste, and this 'mellows' on storage for a few weeks. Prolonged storage, however, especially under conditions in which light and moisture are not excluded, leads to a deterioration in the quality of the tea, ultimately resulting in 'softness', *ie* lacking in briskness and having a 'flat' taste. It is already known that some of the characteristics of tea can be correlated to definite chemical compounds; *eg* Roberts (1962) has shown that there is a direct, although not perfect, relationship between quality and theaflavin content, and between the colour of tea liquors and the relative quantities of theaflavins and thearubigins. Other workers have shown a relationship between amino acids (Bokuchava and Popov 1954; Wickremasinghe 1967; Co and Sanderson 1970) and manganese (Wickremasinghe, Perera & de Silva 1969), with flavour, and the quantity of phaeophytin with the blackness of tea (Wickremasinghe & Perera 1966). The present investigation was designed to determine the nature of the chemical changes which occur during the storage of tea. The study of the chemical changes occurring during storage of tea included analyses for theaflavins, thearubigins, polyphenols, and amino acids, as well as determination of moisture contents. In parallel with, these analyses, the samples were evaluated by a tea taster for variations, during storage, in organoleptic properties.

METHODS AND MATERIALS

Black tea samples, from the same invoice were stored on the bench in (a) a tightly closed, clear glass, bottle and (b) a loosely covered wooden box. The samples were analysed at fortnightly intervals for moisture content, theaflavins and thearubigins, amino acids, total polyphenols, epigallocatechin gallate and epicatechin gallate. Moisture content was determined after drying in an oven at 95° C for 4 hr. Theaflavins and thearubigins were determined by the spectrophotometric method of Roberts and Smith (1961). Amino acids were determined quantitatively according to Moore and Stein (1954), and semi-quantitatively by paper chromatography. Polyphenols were determined colorimetrically (Swain and Hills 1959) using Folin-Ciocalteau reagent for total polyphenols. Epigallocatechin gallate and epicatechin gallate were estimated after elution of the appropriate spots from two-dimensional paper chromatograms, run in butanol-acetic acid-water (6:1:2 v/v) and acetic acid (6% v/v). The eluates were analysed using vanillin reagent (1% vanillin in 70% sulphuric acid).

Each sample was evaluated by the tea taster on the days that extracts for chemical analyses were made.

RESULTS AND DISCUSSION

The conditions of storage was designed in order to obtain data on the relative effects of light and moisture on the changes occurring during storage. Storage in the tightly-covered, clear glass, bottle gave conditions of exclusion of moisture but not light, whereas in the loosely covered wooden box, light but not moisture, was excluded.

Moisture Content

The moisture contents of the two samples with time of storage are shown in Fig. 1. It is seen, as expected, that the increase in moisture content is small in the sample stored in the air-tight bottle, being from 4.2% to 5%, whereas the increase was from 4.2% to 9.9% in the sample stored in the wooden box. Although the tea stored in the box had almost twice as much moisture as that stored in the bottle, the valuations of the two samples (Fig. 2), did not show a great divergence in market prices. This would suggest that high moisture content *per se* does not lead to deterioration of stored teas and that other factors contribute to the 'softening' of teas on storage. As shown in Fig. 1, both samples of tea were reported as being 'soft' after 14 weeks storage. The moisture contents were 4.5% and 7.5% respectively at this time. It is also seen in Fig. 2 that the sample stored with access to air, reached its peak price after two to four weeks, whereas that stored in the air-tight bottle reached its peak after eight weeks. This observation suggests that the 'greenness' of freshly made tea is lost more readily on exposure to the atmosphere rather than otherwise. The chemical reactions responsible for these changes are not known at the present time, but it may be that the combination of the astringent polyphenols with proteins occurs at a faster rate in relatively moist teas than in dry teas.

Recent work (Labuza, Tannenbaum & Karel 1970), has shown that it is the 'water activity' which determines the rates of various reactions involved in food deterioration. Lipid oxidation, leading to rancidity, is most rapid at low water activities, whereas non-enzymatic browning reactions show a peak rate when the water activity increases to an intermediate level. Enzyme activity is also maximal at intermediate levels, whilst growth of micro-organisms occurs only at higher water activities. It will be evident that all of these reactions will be favoured at various stages of storage of tea, and that after prolonged storage it will be the growth of micro-organisms which will have the most pronounced effect. In the particular investigation described here, the valuations of the tea stored in the clear glass bottles were similar, or lower, than those of the tea stored in the wooden box, although the latter has a higher moisture content. This finding suggests that lipid oxidation and non-enzymatic browning reactions are mainly responsible for the deterioration of the tea stored in the clear glass bottle, possibly due to photochemical effects, and that these reactions are initially more detrimental to the valuation of a tea sample than those due to increased moisture alone.

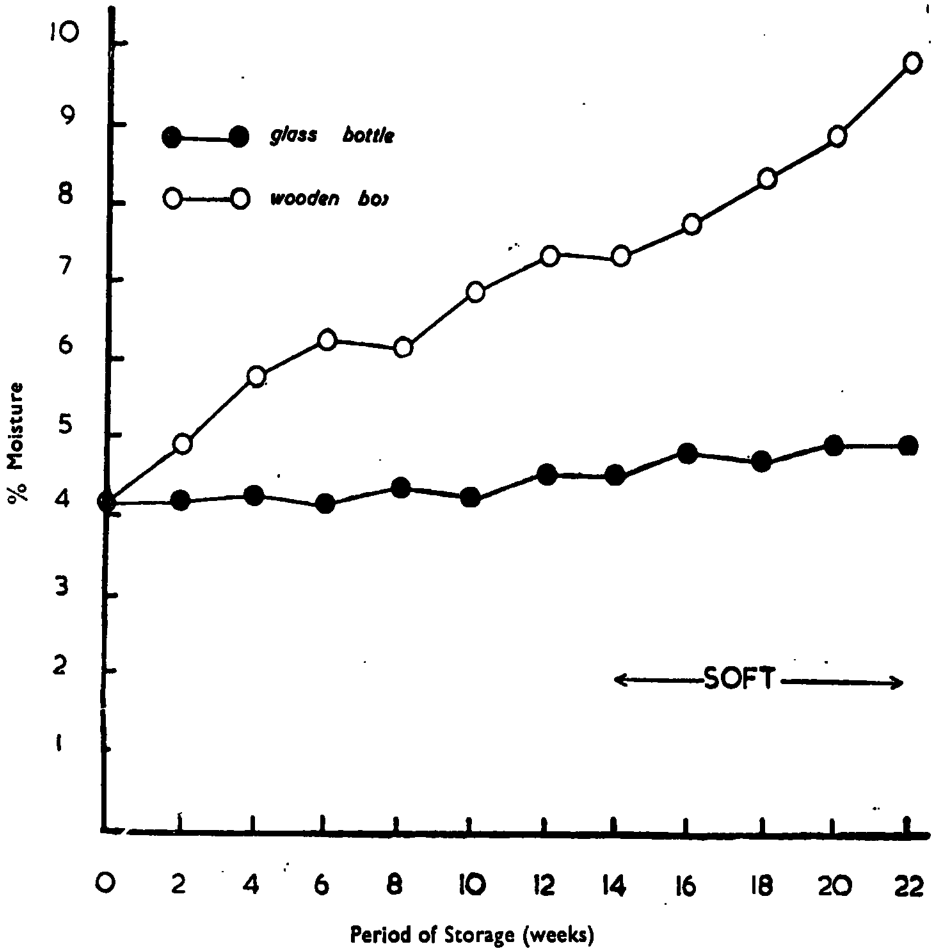

FIG. 1—*Changes in moisture content of black tea samples stored in glass bottle and wooden box*

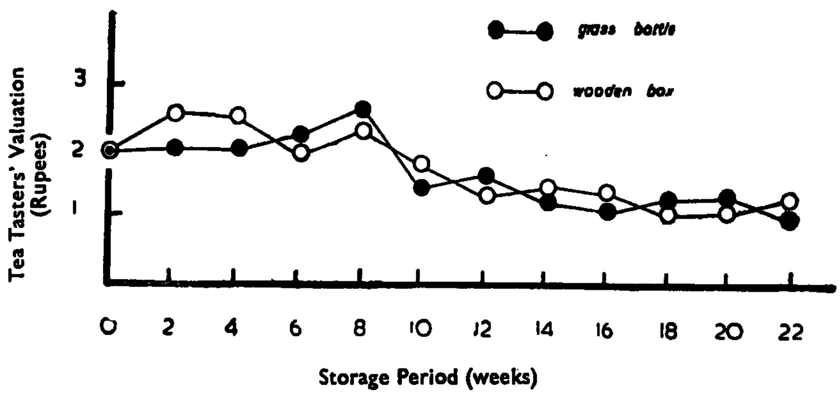

FIG. 2—*Valuations of tea samples after storage in glass bottle and wooden box*

Theaflavins

The changes on storage in theaflavin contents are shown in Fig. 3. The rate of fall of theaflavins is more gradual in the air-tight bottle than in the loosely-covered wooden box, and the final value attained after 20 weeks in the former is higher than in the latter. The valuations of the former were, however, generally slightly lower than the latter. This finding suggests that theaflavin content by itself does not always result in a more highly-valued tea, and that other factors too influence the tea taster's assessment. One could speculate that among these additional factors are groups of compounds which are altered in an undersirable direction by exposure to light in the clear glass bottle.

Amino acids, total polyphenols and thearubigins

The changes of total amino acids, total polyphenols and thearubigins on storage are depicted in Fig. 4. These changes were similar in both the bottle and the wooden box. The amino acids level shows an undulating pattern, and it is of interest to notice that this pattern is the inverse of that of the thearubigin levels. A possible reason for this inverse relationship is that the quantitatively major amino acid of tea, theanine, has been shown to be a constituent of thearubigins (Wickremasinghe & Perera 1966). It would follow, therefore, that a breakdown of thearubigins would result in an increase of theanine, and some evidence in support of this theory was the observation that 'soft' teas, which contain a comparatively low level of thearubigins contained high levels of theanine. It must be surmised, therefore, that there is breakdown and build up of thearubigins during storage, although it is unlikely that the composition of the thearubigins (which is a heterogeneous mixture of coloured complexes) remains unchanged at each stage of storage.

The pattern of change of total polyphenols during storage was similar to that of amino acids in that the levels were undulating and inversely related to that of the thearubigins. Polyphenols too are part of the thearubigin complex (Wickremasinghe & Perera 1966; Brown, Eyton, Holmes & Ollis 1969) and the observation may be additional evidence for breakdown and build-up of thearubigins during storage.

Epigallocatechin gallate and epicatechin gallate

The changes in the quantities of epigallocatechin gallate and epicatechin gallate are shown in Table 1.

TABLE 1 — *Changes in quantities of epigallocatechin gallate (EGCG) and epicatechin gallate (ECG) during storage*

Values expressed as mg/g dry weight of black tea

No. of weeks	*Bottles*		*Box*	
	EGCG	ECG	EGCG	ECG
0	1.04	2.04	1.04	2.04
1	1.30	1.04	1.90	1.70
2	0.60	1.00	0.90	1.44
5	1.30	0.90	1.40	2.00
8	0.84	0.90	0.86	1.34
12	0.99	0.87	0.92	1.60
16	1.02	0.99	1.02	1.00

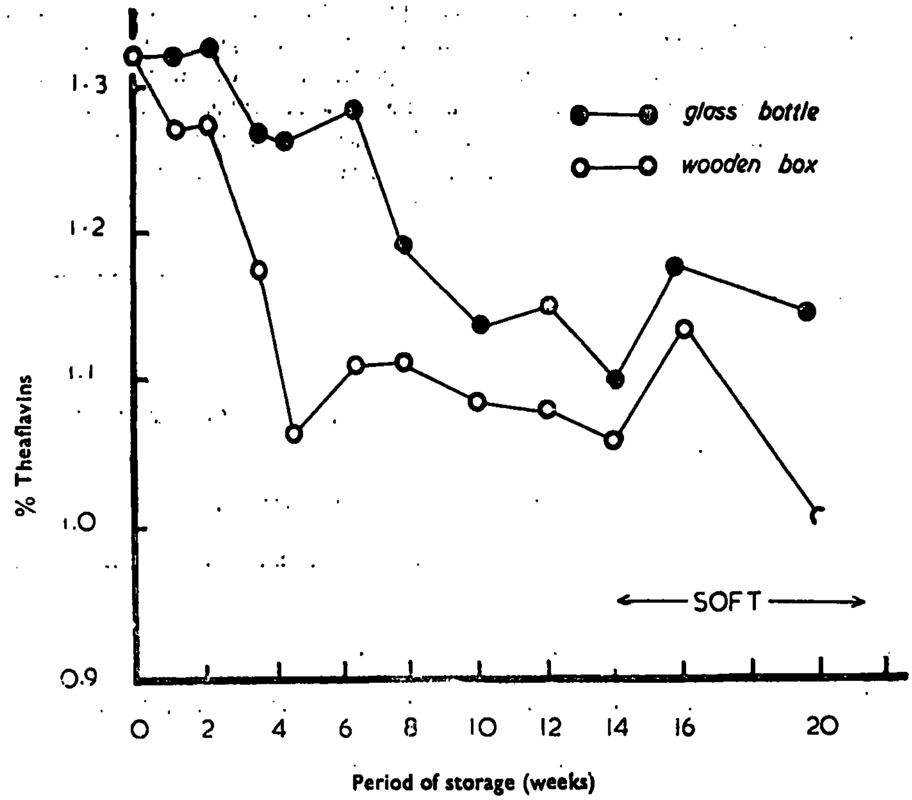

FIG. 3—*Variation of theaflavin content during storage of tea in glass bottle and wooden box*

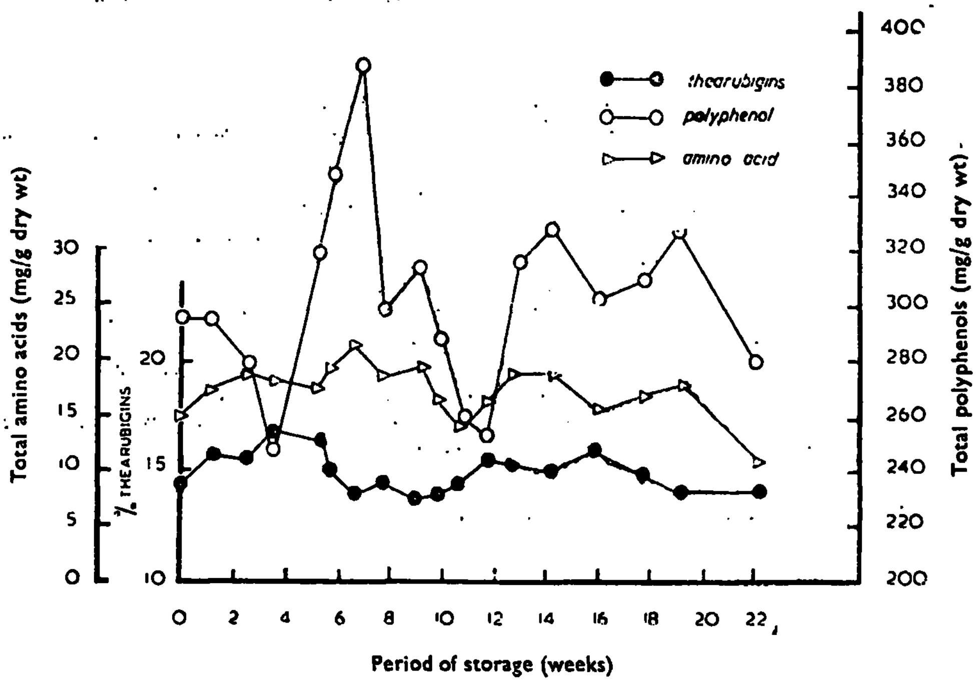

FIG. 4—*Variation in thearubigins, amino acid and polyphenol contents on storage*

These are the most important individual polyphenols in tea, and it is seen that they underwent marked but irregular changes during storage. The final level of epigallocatechin gallate after 16 weeks of storage was not reduced, whereas that of epicatechin gallate was approximately half the original value. This observation suggests that one of the facts contributing to 'softness' of tea may be a reduced level of epicatechin gallate. It is also evident that the levels of both catechins are generaly higher in the tea sample stored in the wooden box than that stored in the bottle. This may be one of the reasons for the tea taster's preference for the tea stored in the box, despite its theaflavin level being lower. It also suggests that the catechins are more photolabile than theaflavins.

SUMMARY

1—High moisture content of made teas is not the sole factor responsible for deterioration on storage.

2—The changes in theaflavin contents on storage are described.

3—The changes in amino acids and polyphenols are inversely proportional to those of thearubigins.

4—Epicatechin gallate levels fall during storage.

5—It is suggested that catechin levels influence the tea taster's assessment.

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