Food Chemistry **13** (1984) 69–77

The Rôle of Added Carbohydrates in Tea 'Cream' Solubilisation

S. Nagalakshmi, M. S. Ramaswamy, C. P. Natarajan & R. Seshadri

Central Food Technological Research Institute, Mysore-570 013, India

(Received: 8 June, 1983)

ABSTRACT

The results of solubilisation studies of the 'cream' of tea infusions are reported. The addition of glucose, sucrose and maltodextrin to hot tea infusions was found to be ineffective. On the other hand, the incorporation of materials such as xylose, sorbitol, glucose, lactose, sucrose and maltodextrin at different levels into the distorted green leaves and subsequent fermentation for different periods resulted in solubilisation of the 'cream' to a large extent, in the following order of efficacy: monosaccharides > disaccharides > polysaccharides. This may be explained by the formation of tannin–carbohydrate–protein (enzyme) complexes in the fermenting leaf.

INTRODUCTION

Cold water-soluble instant tea is becoming an increasingly popular beverage in western countries, especially in the USA where it comprises about 50% of the total sales volume of different varieties of tea and has recorded about a 10% annual growth potential. During the production of cold water-soluble instant tea, a substantial percentage of the valuable components of the tea, known in the tea trade as 'cream', are removed in order to obtain an acceptable product. Such a step affects not only the economics of production of this variety of tea, but also the quality and taste characteristics of the final product as the property of creaming,

Food Chemistry 0308-8146/84/$03·00

considered to be a negative factor here, is a positive quality attribute in black tea evaluation.

Research and developmental efforts in instant tea processing have resulted in the filing of a number of patents in the USA and other countries. These have been catalogued and summarised by Pintauro (1977). Attention has been focused, by a number of patents, on the critical problem of tea 'cream' solubilisation. These involve treatment of the 'cream' with water-soluble sulfite, oxidation with oxygen, hydrogen peroxide, ozone at pH 5·5–7·5, alkalisation of the 'cream' and solubilisation of the 'cream' using the microbial enzyme, tannase.

Several attempts have been made in our laboratories, with varying degrees of success, to solubilise the 'cream' complex. These methods include oxidation methods, solvent decaffeination of black tea, treatment with enzymes like papain and tannase and treatment with various additives like sodium metapolyphosphate, etc. These results will form the subject matter of a subsequent publication. However, our attempts to solubilise the 'cream' were rewarded with some success by treatment of the fermenting tea leaves with different quantities of carbohydrates.

It is now well known that most of the instant teas and tea mixes marketed contain added carbohydrates as fillers, to the extent of 50% or even more. These carbohydrates are added just before the dehydration step. Although the carbohydrates of tea are known to play significant rôles as aroma precursors in black tea manufacture (Sanderson, 1975), no literature is available on the rôle of added carbohydrates in the course of tea fermentation, their effect on the quality parameters of the infusion, etc. In the present investigation the rôle of representative substances such as xylose, glucose, sorbitol, a reducing disaccharide (lactose), a non-reducing disaccharide (sucrose) and a soluble polysaccharide (malto-dextrin) have been investigated with special reference to solubilisation of tea 'cream'.

MATERIALS AND METHODS

Black tea

All experiments were carried out with unblended black tea samples obtained from different tea estates in South India and also with commercially available samples.

Green leaf

Fresh tea leaves brought from a mid-elevation South Indian Tea Estate were stored in a cold room at about 2–4 °C and utilized within a period of 1 week from the date of storage.

Determination of total soluble solids and 'cream'

Ten grams of the black tea sample or its equivalent of fermented green leaf were refluxed for 5 min with 100 ml of boiling distilled water. The hot brew was filtered first through a fine muslin cloth and then through a fast filter paper using a Buchner funnel. A 25 ml aliquot was pipetted into a weighed Petri dish. The aliquot was evaporated to dryness on a steam bath, and heated in an air oven for 1 h at 100 °C, then cooled and weighed. This allowed determination of total soluble solids. The rest of the hot extract was cooled to 5–6 °C in a refrigerator overnight, centrifuged and the solubles determined in an aliquot of the clear extract as above. The differences between the two estimates were taken to indicate the amount of 'cream' separated on cooling.

The experiments were repeated in triplicate and the values were found to be consistent. The mean of the values is presented below.

Incorporation of different carbohydrates into the distorted green tea leaves before fermentation

Green tea leaves were withered and crushed in a laboratory meat mincer. Portions of the minced leaf were treated with xylose, sorbitol, glucose, lactose, sucrose and maltodextrin (dispersed in a minimum quantity of water) at the 4, 5 and 8 % levels on a leaf basis, and thoroughly mixed. An untreated control was also concurrently examined in this experiment. The leaf was spread to about 1 cm thickness in an enamel tray, covered with a wet cloth and allowed to ferment at room temperature. A known quantity of the sample was removed at regular intervals for the determination of the 'cream'.

RESULTS AND DISCUSSION

Preliminary work on the incorporation of the different carbohydrates—glucose, sucrose and maltodextrin—into the tea infusion showed practically

TABLE 1
Effect of Added Carbohydrates on the Separation of the Caffeine–Polyphenol Complex from Tea Infusions

Sample No.	*Percentage carbohydrate added*	*Glucose*	*'Cream' separated*	
			Sucrose	*Maltodextrin*
1	None (control)	0·2	0·4	0·3
2	0·5	0·5	0·6	0·5
3	1·0	0·3	0·5	0·3
4	1·5	0·3	0·4	0·3
5	2·0	0·3	0·5	0·3
6	2·5	0·3	0·4	0·3

no change in the solubilisation of the 'cream', as shown by the results listed in Table 1. It has been shown by Millin *et al.* (1969) that 7% of endogenous polysaccharides only take part in 'cream' formation by forming loosely bound complexes with polyphenolic and proteinaceous materials. These authors have characterised high molecular weight neutral and acidic polysaccharides, especially polygalacturonic acid, as 'cream' components. In the present investigation the absence of any impact on cream formation may be due to the significantly lower molecular weight of the carbohydrates used.

Further experiments were carried out to determine the effect of carbohydrates added to the minced green leaf, followed by fermentation, on the solubilisation of the 'cream'. The data are presented in Table 2. Data presented in this Table represent results obtained from different batches of green leaf obtained from a single tea estate. Monomeric materials like xylose, sorbitol and glucose are more effective in solubilising the tea 'cream'. About 55%, 85% and 70% of the total 'cream' solids were rendered soluble by incorporating xylose, sorbitol and glucose, respectively into the crushed leaf at the 8% concentration level and fermenting for 3 h. The addition of disaccharides such as lactose and sucrose and a polysaccharide like maltodextrin at the same level of concentration (8%) and allowing the fermentation to proceed for 3 h rendered the 'cream' solids soluble to the extent of only 44%, 50% and 35%, respectively. In general, the efficacy of added carbohydrates follows the order monosaccharides > disaccharides > polysaccharides. This shows the importance of the molecular weight—and hence the molecular

TABLE 2

Effect of Added Carbohydrates on the Solubilisation of Tea 'Cream' as a Function of Time of Fermentation

Period of fermentation (min)	*Carbohydrates added*	*Carbohydrates added at:* 4%			6%			8%		
		Per cent 'cream' content Control (a)	Treated (b)	*Per cent total 'cream' solubilised*†	*Per cent 'cream' content* Control (a)	Treated (b)	*Per cent total 'cream' solubilised*†	*Per cent 'cream' content* Control (a)	Treated (b)	*Per cent total 'cream' solubilised*†
0	Xylose	21·0	21·0	—	21·0	21·5	—	21·0	21·6	—
60		21·0	10·0	50·0	21·0	12·6	40·8	21·0	13·8	30·0
120		22·5	7·3	75·0	22·5	10·4	53·8	22·5	12·4	44·9
180		18·6	4·0	78·5	18·6	11·3	39·2	23·0	11·3	55·1
0	Sorbitol	21·7	19·5	5·0	21·7	19·2	5·0	21·7	21·1	—
60		22·0	15·2	25·0	22·0	10·1	50·0	22·0	12·0	40·0
120		22·8	8·9	40·0	22·8	12·0	47·4	22·8	5·2	75·0
180		19·0	6·9	63·4	19·0	16·1	15·5	23·7	3·4	85·0
0	Glucose	22·7	21·0	7·5	16·1	14·5	10·2	21·2	21·0	0·9
60		18·1	12·9	28·5	21·6	17·5	18·9	22·6	11·9	47·6
120		24·5	12·5	48·8	27·1	16·0	40·9	23·4	9·6	48·9
180		19·7	9·8	50·2	14·4	7·4	48·6	25·0	7·5	70·0
0	Lactose	21·6	21·7	—	21·6	21·0	2·8	21·6	22·0	—
60		21·6	5·5	25·0	21·6	11·6	46·3	21·6	17·8	15·0
120		22·8	12·8	40·0	22·8	7·3	67·9	22·8	18·7	17·9
180		18·5	12·0	35·1	18·5	6·9	62·7	22·3	12·3	44·8
0	Sucrose	11·8	10·0	15·3	23·3	16·5	20·1	12·4	11·8	4·9
60		16·7	11·1	33·4	19·9	15·5	21·9	19·3	13·5	30·2
120		20·8	13·9	33·1	23·5	18·6	20·8	17·5	10·0	42·7
180		19·3	11·3	41·5	25·4	16·4	35·3	14·6	7·3	50·0
0	Maltodextrin	18·0	16·5	8·3	19·5	17·4	10·8	24·4	23·3	4·7
60		17·9	14·2	20·8	20·3	14·8	27·3	19·9	14·5	27·0
120		19·3	16·0	17·1	23·5	16·3	30·6	23·5	16·8	20·0
180		18·5	14·3	41·2	25·0	14·3	43·0	15·0	10·3	35·5

† $\frac{((a)-(b))}{(a)} \times 100$.

size—of the carbohydrate moiety participating in the 'cream' solubilisation.

Comparison of the solubilised 'cream' values of added sorbitol and glucose and of added lactose and sucrose showed that there is no significant advantage due to the presence of the free anomeric hydroxyl group, i.e. the free aldehydic group at the first carbon atom of the sugar. Probably the sugar molecules as a whole participate in the 'cream' solubilisation through their hydroxyl groups.

It has been observed by Sanderson & Perera (1965) that there is a marked decrease in the contents of soluble carbohydrates like glucose, sucrose and fructose in made tea in comparison with tea flush and this is evidently manifested during the fermentation stage. Although a portion of such a decrease can be ascribed to the formation of aroma precursors, no conclusive proof has been offered for their enzymatic degradation in the fermenting tea leaf.

The absence of any interaction between the tea 'cream' components and added carbohydrates in the black tea infusions emphasises the rôle played by the tea leaf enzymes, particularly polyphenol oxidase (PPO), present in the fermenting leaves. The catechol oxidase activity of the PPO enzymes is responsible for the conversion of *o*-diphenols into *o*-quinones which constitute the driving force for the enzyme-mediated polymerisation reactions of the flavan monomeric units into polymeric proanthocyanidins (Mayer & Harel, 1979). Now thearubigins have been recognised as the polymeric proanthocyanidins (Brown *et al.*, 1969) and thearubigins, by their interactions with proteins, form the major high molecular weight insoluble components of tea 'cream'. Quesnel (1968), during his investigations on the polymeric proanthocyanidins of *Theabromo cacao*, surmised that the presence of sugars at the 3-position of the leucoanthocyanidin reduces the possibility of further polymerisations.

In view of the above arguments, added carbohydrates seem to play an important rôle in keeping the molecular weight and polymeric nature of thearubigins under certain limits. Two different, but not dissimilar, explanations can be envisaged. According to the first possibility, the *o*-quinones generated from the catechins in the fermenting leaf can interact with hydroxyl groups of the carbohydrates which may further react with the protein (enzyme), leading to carbohydrate–catechin–enzyme complexes. This will prevent further polymerisation of the monomeric catechins into polymeric thearubigins, especially through bisflavonol

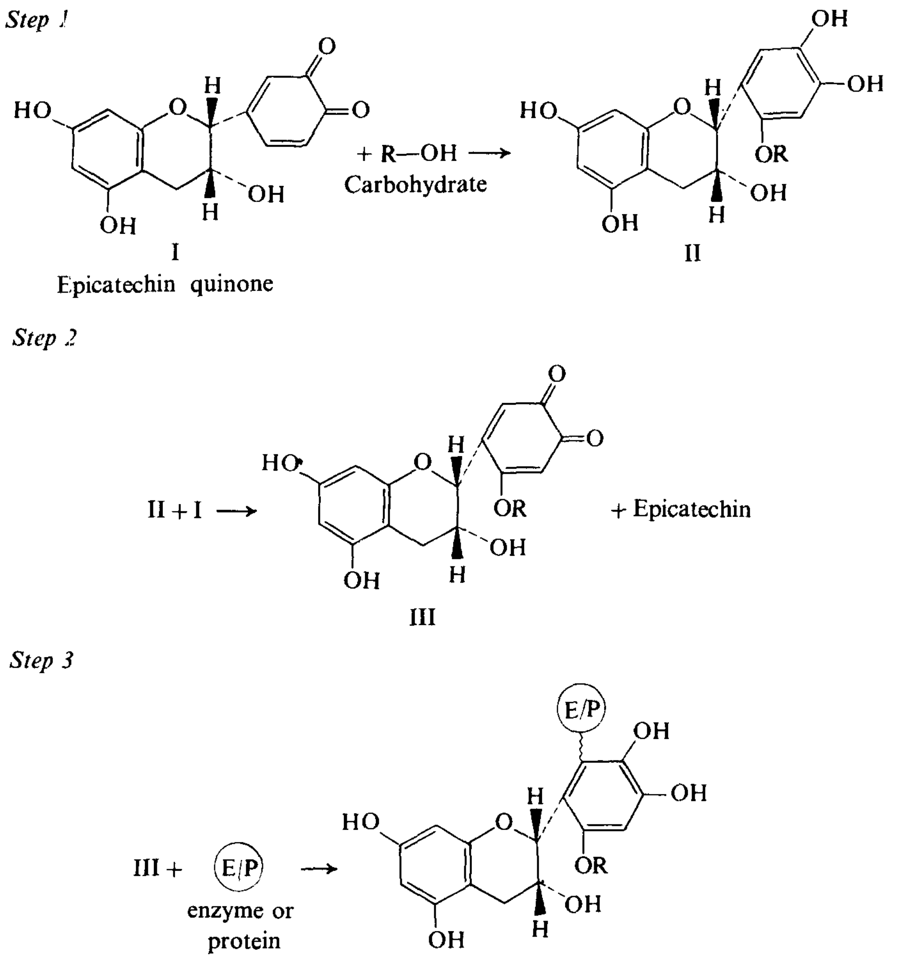

Fig. 1.

intermediates, which is a highly favoured route in such polymerisations. This type of complex formation will also reduce the number of active enzyme sites available for further proanthocyanidin formation. Similar models have been envisaged by Brandt *et al.* (1975) in the case of covalent interactions between carbohydrates and proteins through activated *p*-benzoquinone. Taking epicatechin quinone generated by the action of catechol oxidase on epicatechin, this type of interaction can be schematically represented as shown in Fig. 1.

Even in the event of a protein becoming linked in preference to the enzyme, the molecular size and weight of such a complex will be under control. The formation of insoluble complexes between the tea polyphenol oxidation products and the enzyme protein has been envisaged by Takeo (1966) to explain the decrease of enzyme activity during tea fermentation.

Another interesting possibility arises from the reported occurrence of lignin–carbohydrate complexes identified by Whitmore (1978) and these are deemed to arise as a result of cell wall bound peroxidase mediated polymerisation of phenolic monomers and subsequent complexation with carbohydrates. Lignin–carbohydrate–protein complexes have also been isolated from poplar callus tissue (Fukuda & Kanda, 1976). In the present context, on similar lines it can be presumed that the catechol oxidase endogenous to tea can form a catalytic complex with the catechin and gallocatechin monomeric units which can undergo polymerisation through *o*-quinones; these monomers and polymers can, in turn, form complexes with added carbohydrates, thus preventing further polymerisation. The formation of higher molecular weight polymeric thearubigins, which is an essential requirement for cream formation, is thus controlled.

A great deal of controversy in the research findings exists regarding the localisation of the polyphenol oxidase enzyme activity in the different parts of the tea plant cell—i.e. in the chloroplasts, the mitochondria, the leaf epidermis or in the soluble state (see Wickremasinghe (1978) for a brief review). Whatever its location, there seems to be little doubt regarding the binding of the enzyme sites with polyphenols and carbohydrates resulting in controlled polymerisation (and hence the molecular size), thus leading to reduced 'cream' formation. The differences in the efficacy of the different carbohydrates can then be explained as being due to the efficient diffusion and spatial approach of the lower molecular weight carbohydrates, in comparison with higher molecular weight carbohydrates, to the polyphenols or enzyme sites.

CONCLUSIONS

From the foregoing results it is evident that added carbohydrates are effective in solubilising tea 'cream', the order of efficacy being: monosaccharides > disaccharides > polysaccharides. Since carbohydrates are used as fillers in soluble tea products manufacture, these results are of technological importance.

REFERENCES

Brandt, J., Anderson, L. O. & Porath, J. (1975). Covalent linking of ligands to polysaccharide matrices using benzoquinone, *Biochem. Biophys. Acta*, **386**, 196–202.

Brown, A. G., Eyton, W. B., Holmes, A. & Ollis, W. D. (1969). The identification of thearubigins as polymeric proanthocyanidins. *Nature*, **221**, 742–4; *Phytochem.*, **8**, 2333–40.

Fukuda, T. & Kanda, T. (1976). Studies on the tissue culture of tree cambiums. III. Separation of lignin–carbohydrate–protein complexes from poplar callus tissue, *Mokuzai Gokkaishi*, **22**(2), 564; *Chem. Abstracts*, **85**, 79922.

Mayer, A. M. & Harel, E. (1979). Polyphenol oxidases in plants. *Phytochem.*, **18**, 193–215.

Millin, D. J., Swaine, D. & Dix, P. L. (1969). Separation and classification of the brown pigments of aqueous infusions of black tea, *J. Sci. Fd. Ag.*, **20**, 296–302.

Pintauro, N. D. (1977). *Tea and soluble tea products manufacture*, Noyes Data Corporation, New Jersey, 82–125.

Quesnel, V. C. (1968). Fractionation and properties of the polymeric leucocyanidin of the seeds of *Theobroma cacao*, *Phytochem*, **7**, 1583–92.

Sanderson, G. W. (1975). Black tea and its aroma formation, *Geruch und Geschmacktoffe*. (Drawert, E. (Ed.)), Verlag Hans Carl, Nürnberg, 65–97.

Sanderson, G. W. & Perara, B. P. M. (1965). Carbohydrates in tea plants—I. The carbohydrates of tea shoot tips. *Tea. Quart.*, **36**, 6–13.

Takeo, T. (1966). Tea leaf polyphenol oxidase. Part III. Studies of the changes of polyphenol oxidase during black tea manufacture, *Agric. Biol. Chem.*, **30**, 529–35.

Whitmore, F. W. (1978). Lignin carbohydrate complexes formed in isolated cell walls of callus. *Phytochem.*, **17**, 421–5.

Wickremasinghe, R. L. (1978). Tea. In: *Advances in food research*, Volume 24 (Chichester, C. O. (Ed.)), Academic Press, New York, 229–86.