# 2. Chemical Composition

# 2.1 Compounds present in black tea and its beverage

The precise composition of black tea is markedly influenced by the nature of the green shoots used and by procedures in their subsequent processing which take place in the producing countries. Differences in chemical composition are reflected in the various flavour grades and origins offered on the market, which are from mixed seedling populations with characteristics intermediate between two extreme genotypes, *Camellia sinensis* var. assamica (larger leaves) and *C. sinensis* var. sinensis (small leaves) (Millin, 1987).

The flavour aspects of black and green tea have been described (Millin, 1987), and a review of tea volatiles is available (Bokuchava & Skobeleva, 1986). A listing of the volatile compounds identified in black, Oolong and green tea has been provided by Maarse and Visscher (1986); 404 volatile compounds are listed for black tea, 48 in Oolong tea and 230 in green tea. Groups and subgroups of volatile compounds in black tea leaves are shown in Tables 8 and 9. Table 10 gives a broad tabulation of the components of fresh leaf (Millin, 1987); the structures of some of the components are given in Figure 1. Table 11 gives the composition of black tea beverage.

| Group/subgroup | Number | Numbers of compounds |           |           |  |  |
|----------------|--------|----------------------|-----------|-----------|--|--|
|                | Total  | Aliphatic            | Benzenoid | Alicyclic |  |  |
| Hydrocarbons   | 22     |                      |           | ······    |  |  |
| Saturated      |        | 1                    | 11        | 0         |  |  |
| Unsaturated    |        | 4                    | 1         | 5         |  |  |
| Alcohols       | 39     |                      |           | ÷         |  |  |
| Saturated      |        | 12                   | 3         | 0         |  |  |
| Unsaturated    |        | 19                   | 0<br>0    | 5         |  |  |
| Aldehydes      | 54     |                      | C .       | 0         |  |  |
| Saturated      |        | 11                   | 4         | 0         |  |  |
| Unsaturated    |        | 30                   | 4         | 3         |  |  |
| Hydroxy-       |        | 0                    | 1         | 0         |  |  |
| Methoxy-       |        | 0                    | -<br>1    | Ő         |  |  |

Table 8. Classification of volatile compounds in black tea leaf<sup>a</sup>

| Group/subgroup      | Numbers | s of compounds |           |           |
|---------------------|---------|----------------|-----------|-----------|
|                     | Total   | Aliphatic      | Benzenoid | Alicyclic |
| Ketones             | 48      |                |           |           |
| Mono-               |         |                |           |           |
| Saturated           |         | 10             | 9         | 1         |
| Unsaturated         |         | 11             | 0         | 12        |
| Hydroxy-            |         | 1              | 0         | 1         |
| Di-                 |         |                |           |           |
| Saturated           |         | 2              | 0         | 0         |
| Unsaturated         |         | 0              | 0         | 1         |
| Hydroxy-            |         | 0              | 0         | 0         |
| Acide               | 72      |                |           |           |
| Saturated           | 12      | 38             | 2         | 0         |
| Uncoturated         |         | 28             | 0         | 0         |
| Hudrowy             |         | 20             | 1         | 0         |
| Ora                 |         | 1              | 0         | 0         |
| - Ux0-              | 50      | I              | 0         | Ŭ         |
| Esters              | 52      | 16             | 12        | 2         |
| Saturated           |         | 10             | 12        | 2         |
| Unsaturated         |         | 19             | 1         | 24        |
| Acetal              | 1       | 1              | 0         | -         |
| Nitrogen-containing | 19      |                |           |           |
| Nitriles            |         | 4              | 1         | 0         |
| Amides              |         | 2              | 0         | 0.        |
| Amines              |         |                |           |           |
| Primary             |         | 5              | 2         | 0         |
| Secondary           |         | 0              | 3         | 0         |
| Aza-, Diaza-        |         | 2              | 0         | 0         |
| Sulfur-containing   | 5       |                |           |           |
| Thiols              | -       | 3              | 0         | . 0       |
| Thioether           |         | 1              | 0         | 0         |
| Other               |         | - 1            | 0         | 0         |
| Dhanals             | 11      |                |           |           |
| Manahudroury        | 11      | _              | 8         | -         |
| MONONYUFOXY-        |         | -              | 3         | -         |
| Alkoxy- (ethers)    |         | -              | 5         |           |
| Totals              | 323     | 224            | 67        | 32        |

# Table 8 (contd)

<sup>a</sup>From Maarse & Visscher (1986)

0, none found

-, not applicable

| Group/<br>subgroup | Epoxides | Furans | Pyrans | Lactones | Pyrroles | Benzo-<br>pyrrole<br>(indole) | Pyrazines | Pyridines | Benzo-<br>pyridines<br>(quinolines) | Thiophene | Thiazoles | Benzo-<br>xazoles | Total |
|--------------------|----------|--------|--------|----------|----------|-------------------------------|-----------|-----------|-------------------------------------|-----------|-----------|-------------------|-------|
| Simple             | -        | 1      | -      | _        | _        | 1                             |           | 1         |                                     | 1         |           | 4                 |       |
| Hydrogenated       |          | 3      | 2      | 1        | _        | _                             |           | 1         | -                                   | 1         | -         | 1                 |       |
| Alkyl-             | 6        | 4      | _      | 13       | _        |                               | 11        | -         |                                     | -         | <br>~     | -                 |       |
| Alkoxy-            | -        | 1      | _      | _        |          | _                             | -         | 1         | /                                   | _         | 5         | -                 |       |
| Aldehydes          |          | 2      | -      | -        | _        | _                             | _         | 1         | -                                   | -         | -         | -                 |       |
| Alcohols           | -        | 1      | -      |          | _        | _                             |           | -         | -                                   | -         | -         |                   |       |
| Acyl-              | _        | -      | _      | _        | 3        | _                             | -         | -         | -                                   | -         | -         | -                 |       |
| Aryl-              | -        |        | _      | _        |          | _                             | -         | 1         | -                                   | -         | -         | -                 |       |
| Totals             | 6        | 12     | 2      | 14       | 3        | 1                             | 11        | 16        | 7                                   | 1         | 2<br>7    | -<br>1            | 81    |

Table 9. Classification of heterocyclic (oxygen-, nitrogen- and sulfur-containing) volatile compounds in dry black  $tea^{a}$ 

<sup>a</sup> From Maarse & Visscher (1986)

-, not reported

TEA

| Substance                         | % dry weight |
|-----------------------------------|--------------|
| Flavanols                         | 25           |
| Epi-gallocatechin gallate         | 9-13         |
| Epi-catechin gallate              | 3-6          |
| Epi-gallocatechin                 | 3-6          |
| Epi-catechin                      | 1-3          |
| Others                            | 1-2          |
| Flavonols and flavonol glycosides | 3-4          |
| Flavanediols                      | 2-3          |
| Polyphenolic acids and depsides   | 5            |
| Other polyphenols                 | 3            |
| Caffeine                          | 3-4          |
| Theobromine                       | 0.2          |
| Theophylline                      | 0.04         |
| Amino acids                       | 4            |
| Organic acids                     | 0.5          |
| Monosaccharides                   | 4            |
| Polysaccharides                   | 13-14        |
| Protein                           | 15           |
| Cellulose                         | 7            |
| Lignin                            | 6            |
| Lipids                            | 3            |
| Chlorophyll and other pigments    | 0.5          |
| Ash                               | 5            |
| Volatiles                         | 0.01-0.02    |
|                                   |              |

Table 10. Composition of fresh tea leaf, var. assamica<sup>a</sup>

<sup>a</sup> Adapted from Sanderson (1972), Graham (1984) and Millin (1987)

Black tea beverage differs in composition from fresh leaf in that most of the flavanols and some of the other phenolic materials are converted to the oxidized forms known as theaflavins and thearubigins. The total flavanol level is reduced to 10%, and theaflavins may be present at a level of 1-3% and thearubigins at a level of 10-40% (Graham, 1984; Ullah *et al.*, 1984). Changes in pigmentation and aroma also take place. All other components are virtually unchanged (Millin, 1987).



# Fig. 1. Structures of some important tea components (From Millin, 1987)









(-) epi-catechin gallate, R = H

(-) epi-gallocatechin, R = OH

(without galloyl ester group, position 3) (-) epi-catechin, R = H

Flavanols

(without galloyl ester group, position 3)



#### Flavonols

Kaempferol,  $R_1 = R_2 = H$ Quercetin,  $R_1 = OH$ ,  $R_2 = H$ Myricetin,  $R_1 = R_2 = OH$ 



Theogailin (3-galloylquinic acid)

Н

$$\begin{array}{c} HO_2C - CH - CH_2 - CH_2 - CO \\ 1 \\ NH_2 \\ NHC_2H_5 \end{array}$$

Theanine (y-N-ethylglutamine)





Bisflavanois



Theaflavins

Theaflavin ( $R_1 = R_2 = OH$ ) Theaflavin monogallates ( $R_1 = galloy$ ),  $R_2 = OH$ ) or  $R_1 = OH$ ,  $R_2 = galloyi$ ) Theaflavin digallate ( $R_1 = R_2 = galloyI$ )

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| Substance                 | % dry weight |
|---------------------------|--------------|
| Epi-gallocatechin gallate | 4.6          |
| Epi-gallocatechin         | 1.1          |
| Epi-catechin gallate      | 3.9          |
| Epi-catechin              | 1.2          |
| Flavonol glycosides       | trace        |
| Bisflavanols              | trace        |
| Theaflavins               | 2.6          |
| Theaflavic acid           | trace        |
| Thearubigins              | 35.9         |
| Caffeine                  | 7.6          |
| Theobromine               | 0.7          |
| Theophylline              | 0.3          |
| Gallic acid               | 1.2          |
| Chlorogenic acid          | 0.2          |
| Oxalic acid               | 1.5          |
| Malonic acid              | 0.02         |
| Succinic acid             | 0.1          |
| Malic acid                | 0.3          |
| Aconitic acid             | 0.01         |
| Citric acid               | 0.8          |
| Lipids                    | 4.8          |
| Monosaccharides           | 6.9          |
| Pectin                    | 0.2          |
| Polysaccharides           | 4.2          |
| Peptides                  | 6.0          |
| Theanine                  | 3.6          |
| Other amino acids         | 3.0          |
| Potassium                 | 4.8          |
| Other minerals            | 4.7          |
| Volatiles                 | 0.01         |
|                           |              |

Table 11. Composition of a black tea beverage<sup>a</sup>

<sup>a</sup>Adapted from Graham (1984)

The quantitative data given below generally refer to the content in dry black tea. In order to provide representative values for the content in hot beverage prepared by steeping loose tea (or in tea bags), it is convenient and realistic to assume usage of 13.5 g black tea per litre of hot water, providing six 150-ml cups of consumable brew (or 6.67 cups in all). Thus, 200 cups are available from 450 g black tea, giving 2.25 g black tea per cup. Spiller (1984) assumed an average of 2.27 g per teabag in a cup for US usage.

At a yield of 23-28% w/w soluble solids in black tea from, say, a 3-5 min brew or first withdrawal, 2.25 g per cup would provide 0.3% w/w soluble solids per cup.

#### (a) Nonvolatile compounds

Considerable information is given by Yamanishi (1986) on the changes in composition of both nonvolatile and volatile components during storage under both normal and accelerated conditions.

# (i) Caffeine and other purines

Because brewing techniques vary widely according to cultural customs around the world (Woodward, 1980), estimation of caffeine intake from tea is subject to considerable variation (Stavric *et al.*, 1988). There is little published information on extraction efficiency under household conditions, but examination of the caffeine contents of brewed tea (Bunker & McWilliams, 1979) allowed the Working Group to calculate an extraction efficiency of total solids in the range of 20-30%.

Caffeine has been reported to be present in dry black tea at 3-4% (Millin, 1987), depending upon the type of leaf used (e.g., there is more in fresh shoots). More detailed information is available from Cloughley (1983). In five samples of commercial blended black tea available in the UK, Kazi (1985) found caffeine contents ranging from 2.7-3.2% by a high-performance liquid chromatography procedure.

Table 12 provides estimates of probable caffeine contents per cup of brewed tea, together with directly obtained data. Bunker and McWilliams (1979) provided data on the caffeine content of black tea brews after various brewing times (Table 13). Caffeine tends to form complexes with oxidized polyphenols in black tea (especially theaflavins and thearubigins); when the latter possess gallate ester groupings, such complexes are poorly soluble in cold water.

Kazi (1985) found the obromine at 0.09-0.28% and the ophylline at 0.02-0.06% in dry black tea, which were calculated by the Working Group to correspond to 2.6-8.4 mg and 0.5-1.8 mg per cup.

# (ii) Flavanols and their gallic acid esters

Four flavanols and their gallic acid esters occur in large amounts among the polyphenols present in tea shoots (34% on a dry basis), i.e., epi-gallocatechin and epi-catechin and their corresponding gallates. Normally, only 5-10% of these flavanols survive the processing of black tea, e.g., 1-3% in dry black tea and 3-8% in its total soluble solids (Millin, 1987). Minimal amounts of other flavanols have been reported (Millin, 1987; Hashimoto *et al.*, 1989). Flavandiols, which are originally present in small quantities, disappear totally on processing (Millin, 1987).

| Reference                              | Type of brew                                | Caffeine content<br>(mg/cup) |                                      |
|--|---|------------------------------|--------------------------------------|
|  |   | Average                      | Range                                |
| Kazi (1985)                            | -   |                              | [57-67]ª                             |
| Barone & Roberts (1984)                | Bag<br>Leaf tea<br>Bag<br>Instant tea<br>NS | 42<br>41<br>-<br>28<br>27    | -<br>30-48<br>28-44<br>24-31<br>8-91 |
| US Food and Drug Administration (1984) | NS (US brands)<br>NS (imported brands)      | 40<br>60                     | 20-90<br>25-110                      |

## Table 12. Caffeine content of black tea brews

"Estimates based upon average caffeine content in dry black tea of 3.0% (Kazi, 1985) and range given for 85-100% extraction efficiencies on addition of 150 ml boiling water; 2.25 g tea per cup

NS, not specified; -, not reported

| Type of tea    | Weight of<br>tea leaf (g) | Caffeine content (mg/140 ml; mean $\pm$ SD) with brewing time of: |                 |                 |
|----------------|---------------------------|---|-----------------|-----------------|
|                |                           | 1 min   | 3 min           | 5 min           |
| Bagged         |                           |   |                 |                 |
| Black          |                           |   |                 |                 |
| Brand A        | NS                        | 33±0.4  | 46 <u>+</u> 7.0 | 50±5.0          |
| Brand B        | NS                        | 29 <u>±</u> 0.2   | 44 <u>±</u> 6.0 | 48 <u>±</u> 4.8 |
| Brand C        | NS                        | $21 \pm 1.0$  | 35±1.8          | 39±2.4          |
| Oolong         | NS                        | 13±2.9  | 30±1.7          | 40±1.6          |
| Leaf           |                           |   |                 |                 |
| Black, Brand A | 3                         | 31±1.1  | 38±1.9          | 40 <u>±</u> 6.7 |
| Black, Brand E | 1.7                       | 19 <u>±</u> 2.7   | 25±1.7          | 28±3.3          |
| Oolong         | 2                         | 17 <u>±</u> 0.3   | $20 \pm 0.6$    | 24±0.2          |

# Table 13. Mean caffeine content by brand and brewing time of black and Oolong teas<sup>a</sup>

<sup>a</sup>From Bunker & McWilliams (1979)

NS, not stated; bag used as purchased, one bag per cup of beverage

# (iii) Flavonols and their glycosides

Three flavonols are present: kaempferol (see IARC, 1983a), quercetin (see IARC, 1983b) and myricetin, predominantly as their 3-glycosides. A portion survives the processing stages unchanged and is present in the final product (Millin, 1987).

# (iv) Phenolic acids and depsides

A depside is an ester formed by the condensation of two naturally occurring hydroxy acids. Gallic acid is the most important phenolic acid, while theogallin (3-galloylquinic acid) is the major depside, up to 4% occurring in dry black tea, and is substantially water soluble. The depsides are often referred to as hydrolysable tannins and are the gallo-equivalent of chlorogenic acid in coffee. They are virtually unchanged by processing (Millin, 1987).

# (v) Theaflavins and their gallates

These are of major significance in determining the quality and flavour of tea. They are formed in black tea by oxidation of quinones derived from the epicatechins. They are present to the extent of 1-2% in dry black tea and are substantially water extractable (Millin, 1987).

#### (vi) Bisflavanols

Bisflavanols result from the condensation of *ortho*-quinones, derived from the gallocatechins. They are present at low levels (2-4%) in black tea and are largely water extractable (Millin, 1987).

#### (vii) Thearubigins

Thearubigin is a collective name for the largely unidentified, highly coloured flavanol oxidation products. They are highly heterogeneous in molecular weight and molecular structure and comprise a significant proportion of non-dialysable material. They are often structurally linked to small quantities of peptides or proteins. Their quantity in dry black tea has been given as 10-20% (Ullah *et al.*, 1984), and they are substantially water extractable.

#### (viii) Amino acids and peptides

These compounds are present to a significant extent in black tea (5% on a dry basis); among the amino acids, theanine ( $\gamma$ -N-ethylglutamine) is a major component (Millin, 1987).

#### (ix) Other organic acids

These comprise only a small proportion of black tea (0.5%) and are water extractable (see Table 10).

#### (x) Trace elements

Minerals including fluoride and potassium are present in black and green teas. The tea plant is known to accumulate aluminium and manganese (Graham, 1984).

# (xi) Other nonvolatile compounds

The remaining compounds consist of partially soluble proteins, polysaccharides, lignins and sugars (monosaccharides).

#### (b) Volatile substances

van Straten *et al.* (1983) compiled quantitative data on 56 volatile substances in black tea; 404 such compounds were listed by Maarse and Visscher (1986). Volatile essences (obtained by steam distillation) were reported to account for only 0.02% by weight of black tea, i.e., 200 mg/kg (Sanderson, 1972). It is notable that different groups of workers emphasize different groups of substances as being important to the flavour of tea.

## (i) Carbonyls

van Straten *et al.* (1983) listed quantatitive data for nine aliphatic and two aromatic aldehydes. The quantities reported are generally very small, except that for *trans*-2-hexenal (1.6-25 mg/kg) derived from lipids in the mature leaf; this compound is generally recognized as being undesirable with regard to flavour.

van Straten *et al.* (1983) listed only one ketone and one diketone, both aliphatic, present in very small quantities (0.004-0.2 mg/kg).  $\beta$ -Ionone, a mixed alicyclicaliphatic ketone, is regarded as important for flavour and has been quantified by Skobeleva *et al.* (1979) at 1.3-4.4 mg/kg (0.13-0.44 mg %) in a range of black teas. 2,3-Butanedione (diacetyl) is reported to be present (Wickremasinghe & Swain, 1965) at 0.01-0.2 mg/kg [corresponding to 0.02-0.45  $\mu$ g per cup (2.25 g/cup black tea)]. Small quantities (0.05 mg/l) of methylglyoxal were reported in black tea by Nagao *et al.* (1986); 2.4 mg/kg (0.7  $\mu$ g per serving) were reported in instant tea (Hayashi & Shibamoto, 1985).

#### (ii) Alcohols

Quantitative data are reported by van Straten *et al.* (1983) for 15 aliphatic alcohols, including citronellol and geraniol. Higher quantities of linalool and its oxides, citronellol and geraniol are present in more 'flavourful' teas (e.g., from India) than in lower grades (e.g., from Georgia) (Skobeleva *et al.*, 1979). The listing by von Straten *et al.* (1983) included three other alcohols: benzyl alcohol, 2-phenylethanol and  $\alpha$ -terpineol. Of the simpler aliphatic alcohols, 1-butanol is reported to be present in the largest quantity (12-89 mg/kg); of the others, linalool is reported at 1-29 mg/kg.

## (iii) Volatile acids

Maarse and Visscher (1986) listed 72 volatile acids in black tea. van Straten *et al.* (1983) gave quantitative data for only three of these: formic, acetic and butanoic acids were reported at levels of 0.4, 5.3 and 1.0 mg/kg, respectively, in one sample.

## (iv) Esters

Quantitative data on five aliphatic and three aromatic esters were listed by van Straten *et al.* (1983). The largest reported amount is for hexyl benzoate, at 4-22 mg/kg; methyl salicylate is present at 4.8-4.9 mg/kg.

# (v) Nitrogen compounds

Two amines have been reported to be present in substantial quantities: ethylamine at 288 mg/kg and propylamine at 20-29 mg/kg (van Straten *et al.*, 1983). Although a number of N, N/S and N/O-heterocyclic compounds have been reported (see Table 9), none has been quantified. Yamanishi (1986) reported the occurrence of benzyl cyanide and indole in black tea.

## (vi) Furans

Two complex furans were listed by van Straten *et al.* (1983): one, *cis*-5-(2-hydroxyisopropyl)-2-methyl-2-vinyltetrahydrofuran, was reported to occur at 4-20 mg/kg.

## (vii) Sulfur compounds

Methylthiomethane was reported to be present in black tea at 0.05-0.1 mg/kg (van Straten *et al.*, 1983)

## (viii) Phenols

Eleven phenols were listed as present (Maarse & Visscher, 1986); only phenol was quantified and found at 7-15 mg/kg (Skobeleva *et al.*, 1979).

# (ix) *Epoxides*

*cis*- and *trans*-Linalool oxides were reported to be present in small amounts (Saijo & Kuwabara, 1967). Yamanishi (1986) additionally identified pyranoid and furanoid forms of these two substances. In conjunction with linalool itself, they are regarded as being important for flavour.

# (x) *Hydrocarbons*

Twenty-two hydrocarbons have been reported in black tea (Maarse & Visscher, 1986). Ruschenburg (1985) reported quantities of polycyclic aromatic hydrocarbons ranging from 0.5 to  $3.12 \,\mu$ g/kg in 11 samples of black tea. Four other

samples of black teas had levels ranging from 13.3 to 18.7  $\mu$ g/kg; 51.5-64.6  $\mu$ g/kg were found in five samples of smoked tea. In a 5-min black tea brew, the quantities were less than 0.01  $\mu$ g/l.

#### (xi) Hydrogen peroxide

The hydrogen peroxide content of tea brews was found to increase with the length of incubation and the concentration of tea: for example, a solution of 1 mg/ml tea contained 11.8 nmol/ml [0.4  $\mu$ g/ml] hydrogen peroxide 1 min after it was prepared; a solution of 0.5 mg/ml tea contained 270.4 nmol/ml [9.2  $\mu$ g/ml] hydrogen peroxide after standing at 30°C for about 24 h (Ariza *et al.*, 1988).

## (xii) Summarized data

Table 14 gives estimates of the contents per cup of the groups of volatile compounds considered above. The approximate calculated total is 570 mg/kg (0.06%) in black tea, which is higher than the figure obtained for essence weight (0.02%). [The Working Group suggested that the determined quantity of amines had been overestimated.]

| Group             | Number<br>identified <sup>a</sup> | Number<br>quantified <sup>b</sup> | Total average amount (mg/cup) <sup>c</sup>          |
|-------------------|-----------------------------------|-----------------------------------|---|
| Carbonyls         | 102                               | 13                                | 0.115 (mainly <i>trans</i> -2-hexanol and hexanal)  |
| Alcohols          | 39                                | 18                                | 0.31 (mainly 1-butanol, linalool, 2-phenyl ethanol) |
| Acids             | 72                                | 3                                 | 0.013 (mainly acetic acid)                          |
| Ester             | 52                                | 8                                 | 0.074 (mainly hexyl benzoate)                       |
| Amines            | 12                                | 2                                 | 0.68 (substantially ethylamine)                     |
| Sulfur compounds  | 13                                | 1                                 | 0.0002  |
| Phenols           | 11                                | 1                                 | 0.015-0.034   |
| Furans            | 12                                | 3                                 | 0.05  |
| Epoxides/lactones | 20                                | 2                                 | 0.014   |
| Hydrocarbons      | 22                                | 3                                 | 0.0001  |
| Others            | 49                                | -                                 | -   |
| Total             | 404                               | 54                                | 1.3 (578 mg/kg)                                     |

 Table 14. Estimated content of various groups of volatile compounds in

 brewed black tea

<sup>a</sup> From Maarse & Visscher (1986)

<sup>b</sup>From van Straten *et al.* (1983)

Calculated by the Working Group assuming 100% extraction from 2.25 g of dry black tea

Table 15 provides quantitative data on the most abundant aroma compounds in a high-quality black Darjeeling tea (Schreier & Mick, 1984).

| Component                     | Quantity (mg/kg) |
|-------------------------------|------------------|
| Linalool oxides               | 23               |
| Linalool                      | 18               |
| Geraniol and benzyl alcohol   | 7.5              |
| Methyl salicylate             | 5.5              |
| cis-3-Hexen-1-ol              | 4.2              |
| 2-Phenylethanol               | 3.3              |
| trans-2-Hexenal               | 2.5              |
| Hexanal                       | 1.7              |
| 1-Penten-3-ol                 | 1.6              |
| trans-2-penten-1-ol           | 1.3              |
| Phenylacetaldehyde            | 1.3              |
| trans, trans-2, 4-Heptadienal | 1.2              |
| trans-2-Hexen-1-ol            | 1.2              |

Table 15. Principal aroma components in a dry Darjeeling tea<sup>a</sup>

"From Schreier & Mick (1984)

#### (d) Additives and contaminants

Allowable levels of pesticide residues are given by the US Department of Agriculture (1989). Most teas in international trade comply with these regulations.

Some black tea has traditionally been flavoured with various natural agents; the most famous is the 'Earl Grey' blend, prepared by the addition of oil of bergamot (main constituent, linalool) (Millin, 1987). Another popular additive is jasmine flowers, added at the time of drying to both black and green tea. Lapsang Souchong teas are smoked during processing (Graham, 1984).

# 2.2 Compounds present in green tea and its beverage

The flavour of the green tea beverage is considered to depend upon a suitable balance between the largely unoxidized polyphenols and amino acids, especially theanine (Graham, 1984). The volatile fraction is derived from the original volatiles present in the fresh leaf and pyrolysis products produced during firing. Like black tea, the most important desirable flavour characteristics are associated with higher-boiling terpenid and aromatic substances (Millin, 1987). A total of 230 volatile compounds has been identified in green tea (Maarse & Visscher, 1986).

The quantitative data presented below refer to the content in dry green tea, assuming that the quantity of green tea used per cup is similar to that for black tea, i.e., 2.25-3.0 g.

(a) Nonvolatile compounds

(i) *Caffeine* 

The caffeine content of green tea is similar to that of black tea (Table 16).

Table 16. Mean caffeine content by brand and brewingtime of green tea $^a$ 

| Type of tea | Weight of tea<br>leaf (g) | Caffeine $\alpha$ mean $\pm$ S | Caffeine content (mg/140 ml;<br>mean $\pm$ SD) with brewing time of: |                 |  |
|-------------|---------------------------|--------------------------------|--|-----------------|--|
|             |                           | 1 min                          | 3 min  | 5 min           |  |
| Bagged      |                           |                                |  |                 |  |
| Brand A     | NS                        | 19±1.0                         | 33±2.7   | 36±2.7          |  |
| Brand B     | NS                        | 9 <u>±</u> 0.2                 | $20 \pm 0.2$   | $26 \pm 0.2$    |  |
| Leaf        |                           |                                |  |                 |  |
| Brand A     | 2.7                       | $28 \pm 1.5$                   | 33±5.8   | $35 \pm 1.6$    |  |
| Brand C     | 1.2                       | 15 <del>±</del> 0.1            | -  | $20 \pm 1.8$    |  |
| Pan-fired   | 1.7                       | 14 <u>±</u> 0.9                | 20±2.7   | 21 <u>±</u> 3.5 |  |

"From Bunker & McWilliams (1979)

NS, not stated; bag used as purchased, one bag per cup of beverage

## (ii) Flavanols, flavonols and their glycosides

As no 'fermentation' is involved, there is very little polyphenol oxidation; polyphenols amount to 38% of the total soluble solids of dry extract (Graham, 1984).

#### (iii) Phenolic acids and their depsides

Depsides are present in the green tea shoots and are largely unchanged by processing (Millin, 1987).

## (iv) Theaflavins and thearubigins

Green tea has little or none of these transformation products.

(v) Ascorbic acid

Ascorbic acid (vitamin C) is present in green tea at an average level of 2.0-2.5 g/kg (Yamanishi, 1986).

## (vi) Amino acids and peptides

Theanine ( $\gamma$ -N-ethylglutamine) is the most important constituent of green tea, constituting some 4.70% of the dry weight of extract. Other free amino acids are present, in particular glutamic acid (0.50%), aspartic acid (0.50%) and arginine (0.74%); others are present to a total of 0.74% (Graham, 1984).

#### (b) Volatile compounds

van Straten *et al.* (1983) listed data on 113 volatile compounds in green tea. The total volatile compound content is reported to be one-third to one-quarter of that in black tea, and quantitative data are available for a large number of compounds.

### (i) Carbonyls

van Straten *et al.* (1983) reported quantitative data for three aliphatic aldehydes, one aromatic aldehyde,  $\beta$ -cyclocitral and safranal. Only *trans*-2-hexenal was reported to be present in a significant quantity, i.e., 10 mg/kg. These authors also reported quantitative data for 13 complex ketones and diketones, all present in very small quantity, except  $\beta$ -ionone at 0.4-6.4 mg/kg. Traces of methylglyoxal have been reported in green tea (Nagao *et al.*, 1986).

## (ii) Alcohols

van Straten *et al.* (1983) gave quantitative data for 26 alcohols, including geraniol, nerol and linalool. The concentration of geraniol ranged from 0.2 to 13.8 mg/kg, and that of linalool from 0.4 to 50 mg/kg.

#### (iii) Acids

van Straten *et al.* (1983) reported that six aliphatic acids up to decanoic occurred at low levels.

#### (iv) Esters

van Straten *et al.* (1983) reported data for 11 mainly aliphatic esters, including methyl jasmonate (0.2 mg/kg).

#### (v) Nitrogen compounds

van Straten *et al.* (1983) reported ethylamine at 210-457 mg/kg and diphenylamine at 1.5 mg/kg. They also reported data on four pyrroles, two indoles and three pyrazines, presumably arising from the 'firing' stage, but in small quantities, except for indole at 1.2-9.7 mg/kg.

#### (vi) Furans

The same furans as in black tea are reported to be present in very small quantities.

#### (vii) Others

van Straten *et al.* (1983) reported figures for five lactones, benzylcyanide, three phenols, 1,2,4-trichlorobenzene and three epoxides. They also reported figures for 20 hydrocarbons, of which  $\delta$ -cadinene occurred in the largest amount (23.5 mg/kg).

#### (viii) Summarized data

Belitz and Grosch (1986) listed the percentages of volatile compounds, ranging from linalool (19.9%) and  $\delta$ -cadinene (9.4%) down to heptanol (0.1%). Table 17 gives estimates of the contents per cup of the groups of volatile compounds considered above.

| Group               | Number<br>identified <sup>a</sup> | Number<br>quantified <sup>b</sup> | Total average amount (mg/cup) <sup>c</sup> |
|---------------------|-----------------------------------|-----------------------------------|--|
| Carbonyls           | 55                                | 19                                | 0.11                                       |
| Alcohols            | 34                                | 15                                | 1.1  |
| Acids               | 15                                | 6                                 | 0.007                                      |
| Esters              | 20                                | 11                                | 0.0018                                     |
| Amines              | 3                                 | 2                                 | 0.9 (mainly ethylamine)                    |
| Pyroles and indoles | 10                                | 6                                 | 0.03                                       |
| Pyrazines           | 23                                | 3                                 | 0.0018                                     |
| Phenols             | 14                                | 3                                 | 0.0039                                     |
| Furans              | 8                                 | 7                                 | 0.048                                      |
| Lactones            | 5                                 | 5                                 | 0.006                                      |
| Epoxides            | 6                                 | 3                                 | 0.018                                      |
| Hydrocarbons        | 30                                | 20                                | 0.15                                       |
| Others              | 7                                 | 28                                | 0.009                                      |
| Total               | 230                               | 128                               | 2.4  |

 Table 17. Estimated content of various groups of volatile compounds in brewed green tea

"From Maarse & Visscher (1986)

<sup>b</sup>From van Straten et al. (1983)

Calculated by the Working Group assuming 100% extraction from 3 g green tea

Kosuge *et al.* (1981) determined the aroma composition in high-quality pan-fired green Japanese teas. One example is shown in Table 18.

# Table 18. Volatile compounds in a Japanese pan-fired green tea<sup>a</sup>

| Compound                                   | %    |
|--|------|
| Geraniol                                   | 17.9 |
| Linalool oxides                            | 16.1 |
| Linalool                                   | 9.5  |
| Nerolidol                                  | 8.8  |
| <i>cis</i> -Jasmone                        | 7.5  |
| 2,6,6-Trimethyl-2-hydroxycyclohexane-1-one | 7.0  |

# Table 18 (contd)

| Compound                | %   |
|-------------------------|-----|
| β-Tonone                | 5.5 |
| Benzyl alcohol          | 4.7 |
| sis-3-Hexenyl hexanoate | 3.5 |
| 5,6-Epoxy-β-ionone      | 2.7 |
| -Penten-3-ol            | 2.7 |
| x-Terpineol             | 2.2 |
| is-3-Hexen-1-ol         | 2.0 |
| Acetylpyrrole           | 1.8 |
| -Phenylethanol          | 1.3 |
| is-2-Penten-1-ol        | 1.1 |
| entanol                 | 0.7 |
| 2,5-Dimethylpyrazine    | 0.6 |

<sup>a</sup> From Kosuge et al. (1981)