

## On the Formation of Black Tea Aroma

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Black tea aroma is formed during the 12 to 24 hr taken for the manufacture of black tea from fresh green tea flush. Biochemical changes occurring during the withering stage are preparative for tea fermentation which is characterized by the atmospheric oxidation of the tea flavanols catalyzed by an endogenous catechol oxidase. The oxidized flavanols are strong oxidizing agents which may oxidize other compounds present, forming volatile compounds that contribute to tea aroma: amino acids, carotenoids, and unsaturated fatty

acids undergo changes by this mechanism. During firing (drying) further oxidative changes take place, and black tea aroma acquires its particular character. Over 140 compounds have been identified in black tea aroma, but none of these compounds is distinctly black tea-like. Whether a critical tea aroma constituent remains to be identified or whether tea aroma is determined by a peculiar balance of several components has not yet been determined.

Tea is one of the most widely consumed beverages in the world. About 2.4 billion pounds of tea were produced in 1971 in tropical and subtropical areas around the world, and the tea produced is marketed in virtually every country on earth (World Coffee & Tea, 1972). The United States is not often thought of as a tea-drinking nation, but the United States had a per capita consumption of 0.74 lb of tea in 1971, making this country the sixth greatest tea-consuming country in the world.

The popularity of tea as a beverage rests firmly on its pleasant flavor which so many people find appealing and its mildly stimulating effects. The flavor of tea is determined by the combined effects of the nonvolatile solids extractable from tea leaf, which amount to about 25 to 35% of the tea leaf under normal brewing conditions, and the very complex volatile fraction of the tea leaf extract, which probably constitutes less than 0.1% of the tea leaf dry weight. The contribution of the nonvolatile solids present in a cup of tea to the taste of the beverage was reviewed by Millin *et al.* (1969) and will not be dealt with further in this paper. Rather, the subject of this paper will be the much smaller fraction of the tea beverage, which is composed of volatile compounds and which accounts for the aroma and much of the flavor of tea. Further, this paper will concentrate on reviewing our current understanding of the chemistry and biochemistry of black tea aroma formation. Papers reviewing the composition of tea aroma *per se* have been published by Yamanishi (1967, 1968), Bondarovich *et al.* (1967), and Sanderson (1972a). Reviews of tea chemistry as a whole have been prepared by Roberts (1962), Stahl (1962), Millin and Rustidge (1967), Bokuchava and Skobeleva (1969), Eyton (1972), and Sanderson (1972a).

It should be pointed out that there are several types of tea (*e.g.*, green tea, oblong tea, black tea, etc.), each with several subtypes (Eden, 1965; Harler, 1964). All types of tea are prepared from essentially the same starting material, namely, the rapidly growing shoot tips of the tea plant *Camellia sinensis* (L.) O. Kuntze, with the primary differences between the types being introduced as a result of the processing conditions used to manufacture the finished product (Eden, 1965; Eyton, 1972; Hainsworth, 1969; Harler, 1963). This review shall deal only with the problem of black tea aroma formation inasmuch as this is the product of primary importance in the so-called Western world, and it is the problem of greatest familiarity to the authors.

### WHAT IS BLACK TEA AROMA?

The powerful modern analytical tools, especially gas-

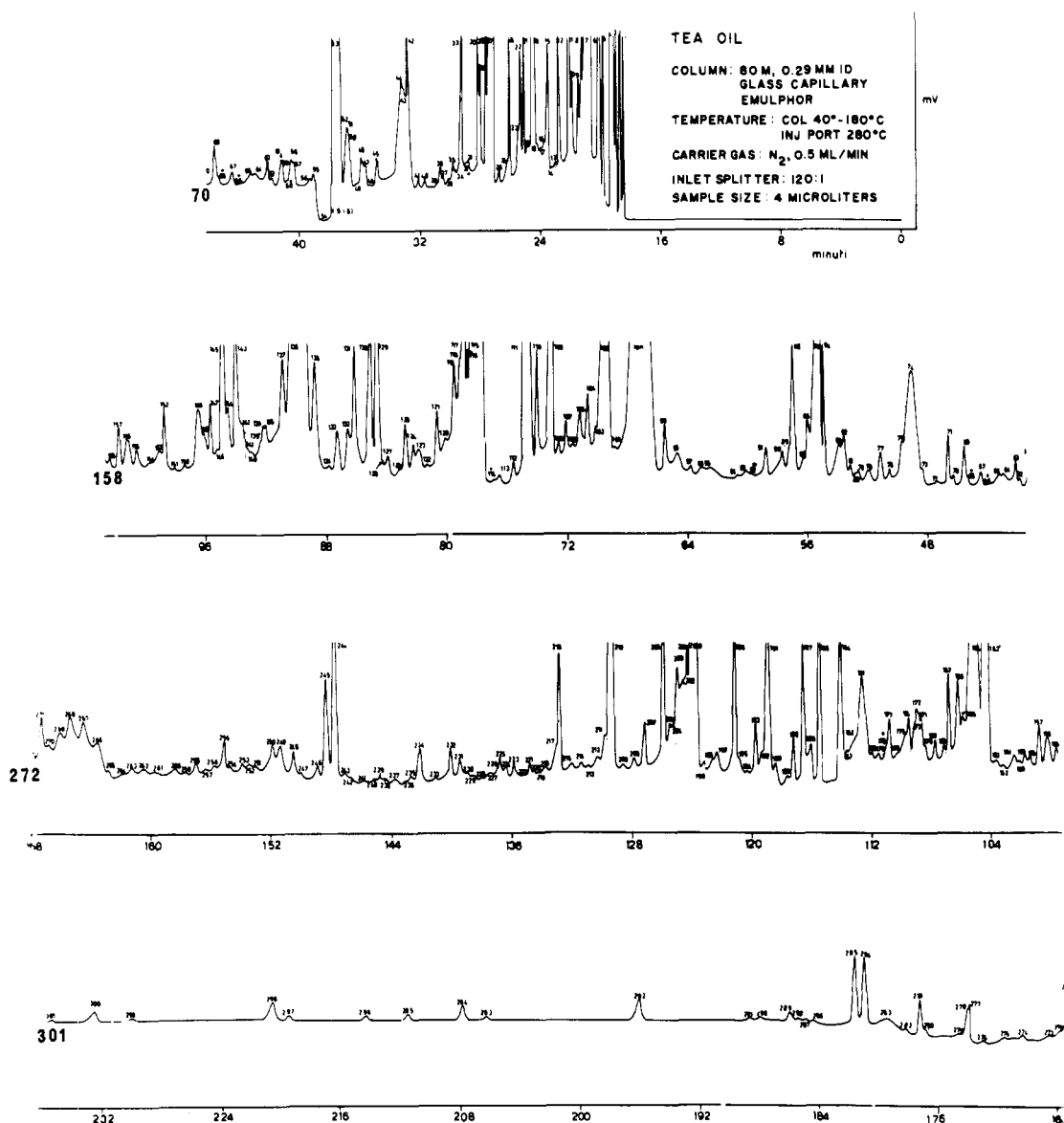
liquid chromatography and mass spectroscopy, have revealed that tea aroma is a most complex mixture of substances. An excellent example of the expertise which has been applied to the study of tea aroma is the gas-liquid chromatogram shown in Figure 1, supplied by M. A. Giaturco. Note that the chromatogram shows resolution of tea aroma into 301 components although identifications of only 145 compounds have been reported in the literature (Table I; Bondarovich *et al.*, 1967; Bricout *et al.*, 1967; Müggler-Chavan *et al.*, 1966, 1969; Sanderson, 1972a; Yamanishi, 1967, 1968; Yamanishi *et al.*, 1972).

The types of compounds which have been identified in black tea aroma are summarized in Table I. Examination of this table reveals that carbonyl compounds predominate, followed closely by alcohols and acids. Strikingly few of either terpenoid compounds, esters, or pyrolytic products [*e.g.*, pyrazines and furans (Fagerson, 1969; Reynolds, 1970)] have been found in black tea aroma. Four observations relating to the chemical nature of black tea aroma appear to be particularly important to this review. First, none of the identified black tea aroma constituents (Table I; Sanderson, 1972a) are especially tea-like by themselves (Dukker *et al.*, 1972; Yamanishi, 1968). The report (Ina *et al.*, 1968) that theaspiron (see Table III, footnote *g*) has a distinctly black tea-like character has yet to be verified. Second, as Bondarovich *et al.* (1967) pointed out, there are many unidentified constituents of black tea aroma, and some of these trace constituents may play a most important role in determining the flavor of black tea. Third, black tea aroma is formed during the black tea manufacturing process. Many of the compounds identified in black tea aroma have not been found in fresh green tea flush (see Table 13 in Sanderson, 1972a). These results suggest that new compounds are formed during the black tea manufacturing process which are not present in fresh green tea leaf material, but it remains for more definitive comparative studies to verify these results. And fourth, the relative amounts of black tea aroma constituents vary markedly between different teas (Reymond *et al.*, 1966; Yamanishi *et al.*, 1968a,b); yet all black teas are generally recognized as black tea. This is suggestive of one or a few critical black tea aroma constituents. These four points must be kept in mind as we go on to consider the available information on black tea aroma formation.

### THE BLACK TEA MANUFACTURING PROCESS

The black tea manufacturing process is outlined in Figure 2 [more detailed descriptions of this process are found in accounts by Eden (1965), Eyton (1972), Harler (1963), Hainsworth (1969), and Keegel (1958)]. The process is normally carried out on the tea estate on which the tea leaf was grown. The entire process, from plucking the leaf

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**Figure 1.** Gas-liquid chromatogram of tea aroma. This excellent chromatogram was supplied by M. A. Gianturco of The Coca-Cola Company, Atlanta, Ga. (figure used with permission). Note that the chromatogram shows resolution of tea aroma into 301 components, although identification of only 145 components has been reported in the literature (see Table I).

to firing (drying) the fermented tea leaf, may take from 10 to 18 hr. It is noteworthy that the aroma of the tea leaf undergoes a continuous change during the manufacturing process that has been described by Harler (1963) in the following words: "The aroma of the leaf changes as fermentation proceeds. Withered leaf has the smell of apples. When rolling begins this changes to one of pears, which then fades and the acrid smell of green leaf returns. Later, a nutty aroma develops and finally a sweet smell, together with a flowery smell if flavour is present."

#### THE FRESH TEA LEAF AND THE ROLE OF WITHERING

At the time tea leaf is plucked (harvested), its potential to be converted to a quality black tea is largely fixed. That is, the amounts of the starting materials involved in the production of a black tea product—namely, the amount of enzymes, tea flavanols, aroma constituents, aroma precursors, etc. (Sanderson, 1972a)—are fixed by the removal of the tea leaf from the tea plant. As discussed below, biosynthetic reactions which take place during the black tea manufacturing process probably do contribute to black tea aroma, but the relative significance of this contribution remains to be determined. While subsequent manufacturing operations are carried

out mainly according to empirical rules, it is the objective of those operations to manipulate the tea leaf so as to maximize the quality of the final black tea product.

In traditional, or orthodox, black tea manufacturing processes (Eden, 1965; Eyton, 1972; Hainsworth, 1969; Harler, 1963), the plucked tea leaf is first withered to reduce its moisture content from about 75% in the freshly-plucked leaf to about 55 to 65% in the withered leaf. This process normally takes about 4 to 16 hr, depending on the local conditions and the type of equipment used.

The main purpose of the withering process is probably to render the tea leaf in a physical condition which is most suitable for subsequent stages of manufacturing, but biochemical changes also take place which appear to have an effect on the quality of the product (Sanderson, 1964b, 1972a). The biochemical changes which have been studied include: (a) the breakdown of protein to amino acids (Roberts and Sanderson, 1966; Roberts and Wood, 1951); (b) an increase in caffeine (Sanderson, 1964b; Wood and Chanda, 1955); (c) an increase in sugars (Sanderson and Perera, 1965); (d) changes in the level of organic acids (Sanderson and Selvendran, 1965); (e) changes in the level of catechol oxidase activity (Sanderson, 1964a; Takeo, 1966); and (f) an increase in cell membrane per-

## Operations (biochemical and chemical changes important to black tea aroma formation)

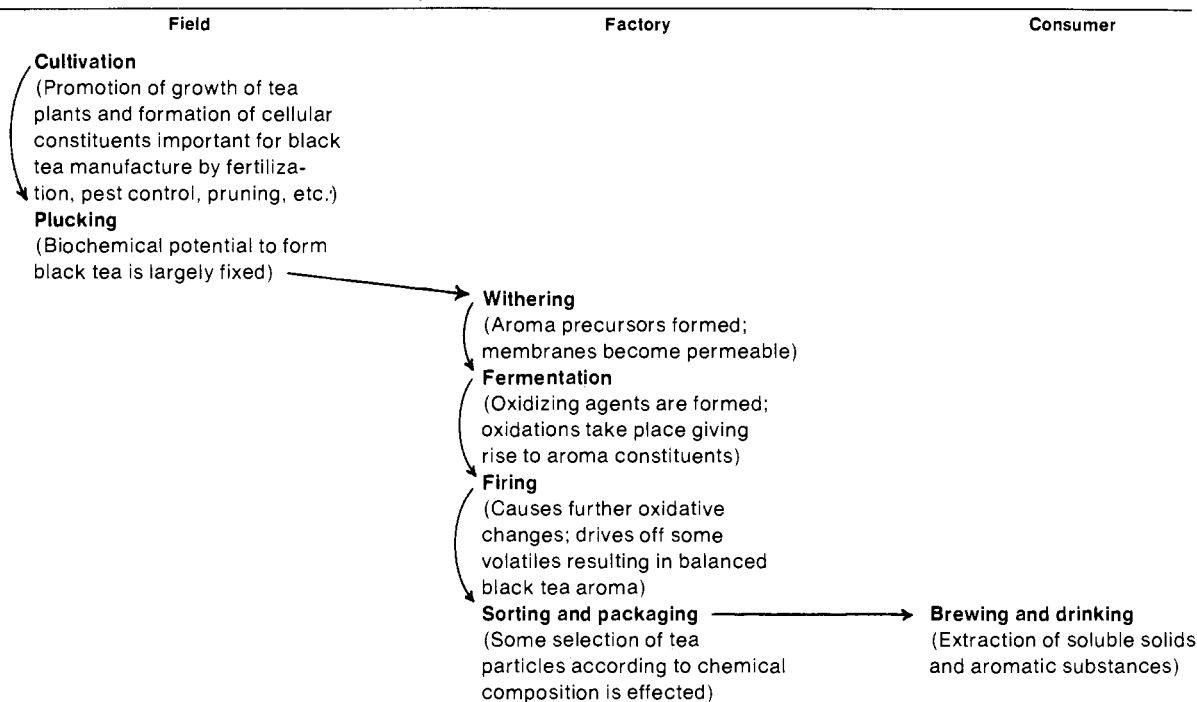


Figure 2. Outline of black tea manufacturing process from cultivation of fresh green tea flush to brewing of black tea.

Table I. Summary of Compounds Present in Black Tea Aroma<sup>a</sup>

Class	Examples	Number of compounds identified <sup>a</sup>
Hydrocarbons	Limonene	7
Alcohols	Phenylethanol	36
	Linalool	
Carbonyls	Geraniol	46
	<i>trans</i> -2-Hexenal	
Acids	Phenylacetaldehyde	21
	$\beta$ -Ionone	
Esters and lactones	Isovaleric	18
	Benzoic	
Others	Methyl benzoate	17
	Geranyl formate	
	<i>o</i> -Cresol	145
	Dimethyl sulfide	
	<i>N</i> -Ethylformylpyrrole	
	Total identified	

<sup>a</sup> Summarized from complete list of identified compounds compiled by Sanderson (1972a) plus nine new compounds recently identified by Yamanishi *et al.* (1972).

meability (Sanderson, 1968). Changes a through d are presumed to affect the outcome of the black tea manufacturing process because they affect the amounts and kinds of aroma precursors available in the tea leaf material. Change e is important because the enzyme catechol oxidase appears to have a central role in the overall black tea conversion process. This is discussed more fully in the following section. Finally, change f is thought to be important because the cell membranes must be permeable before tea fermentation, with the attendant formation of black tea aroma, can take place generally throughout the tea leaf tissues (Sanderson, 1964b, 1968, 1972a).

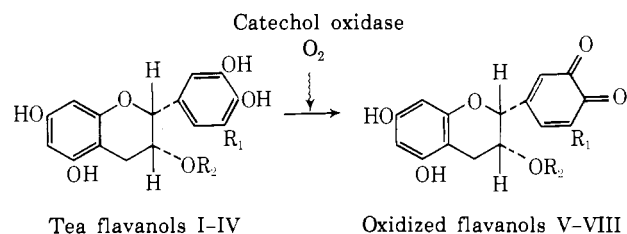


Figure 3. The primary reaction of tea fermentation, namely the catechol oxidase-catalyzed oxidation of the tea flavanols (I-IV): I, (-)-epicatechin; R<sub>1</sub> = R<sub>2</sub> = H; II, (-)-epicatechin-3-gallate; R<sub>1</sub> = H, R<sub>2</sub> = 3,4,5-trihydroxybenzoyl; III, (-)-epigallocatechin; R<sub>1</sub> = OH, R<sub>2</sub> = H; IV, (-)-epigallocatechin-3-gallate; R<sub>1</sub> = OH, R<sub>2</sub> = 3,4,5-trihydroxybenzoyl; V-VIII, 3',4'-orthoquinones of I-IV, respectively.

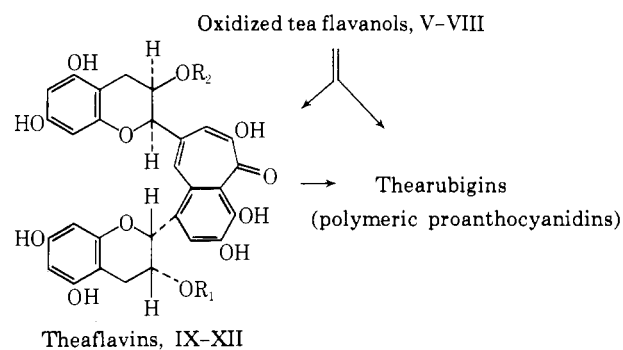


Figure 4. Condensation of oxidized tea flavanols (V-VIII) produces theaflavins (IX-XII) and thearubigins (polymeric proanthocyanidins) (Brown *et al.*, 1969a,b) which are the principal colored substances of black tea: IX, theaflavin; R = R' = H; X, theaflavin gallate A; R<sub>1</sub> = H, R<sub>2</sub> = 3,4,5-trihydroxybenzoyl; XI, theaflavin gallate B; R<sub>1</sub> = 3,4,5-trihydroxybenzoyl, R<sub>2</sub> = H; XII, theaflavin digallate; R<sub>1</sub> = R<sub>2</sub> = 3,4,5-trihydroxybenzoyl.

Table II. Volatile Aldehydes Produced from Amino Acids during Black Tea Manufacture

Amino acid	Odor formed according to Bokuchava and Popov (1954)	Volatile aldehyde formed	
		Compound	Reported by <sup>a</sup>
Glycine	None	Formaldehyde	(b)
Alanine	Flowery	Acetaldehyde	(a,b)
Valine		Isobutyraldehyde	(a,b,c)
Norleucine	Spicy		
Leucine		Isovaleraldehyde	(a,b,c)
Isoleucine		2-Methylbutanal	(b,c)
Methionine		Methional	(a,b)
Phenylalanine	Rose-like	Phenylacetaldehyde	(b,c)
Cystine	None		
Aspartic acid		None	(c)
Glutamic acid	Flowery	None <sup>b</sup>	(b,c)
Glutamine		None	(c)
Threonine	Winy	None	(c)
Serine		None	(c)
Tyrosine	Unpleasant	None	(b)
Tryptophane	Unpleasant	None	(b)
Theanine		None	(c)

<sup>a</sup> Summarized from results published by: (a) Nakabayashi (1958a,b,c); (b) Saijo and Takeo (1970a,b); and (c) Co and Sanderson (1970). <sup>b</sup> Succinimide has been shown to form from glutamic acid by Moss *et al.* (1972).

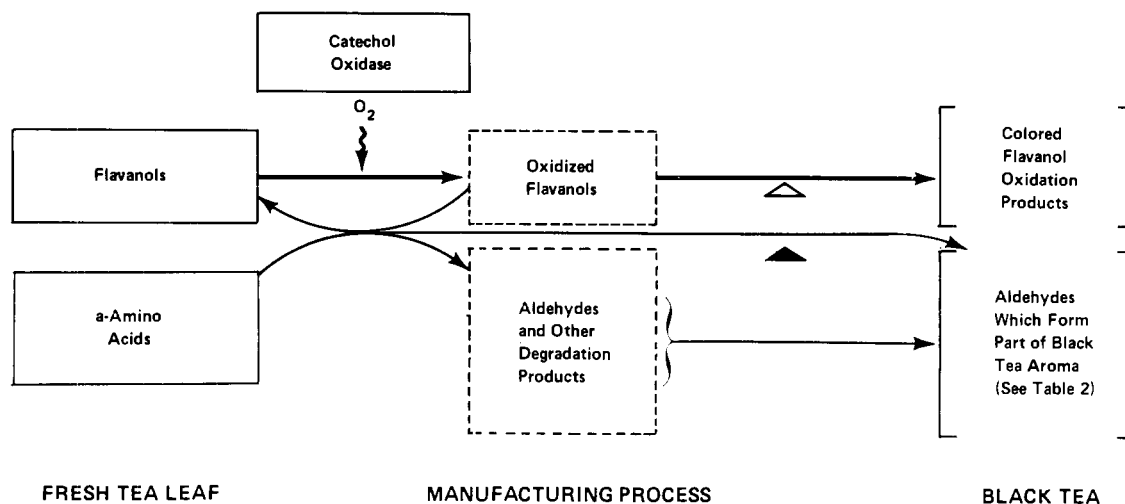


Figure 5. Scheme showing formation of carbonyl compounds from amino acids during tea fermentation.  $\Delta$ , transformations resulting from enzymic oxidations and firing.  $\blacktriangle$ , transformations resulting from firing. (Adapted from Co and Sanderson, 1970.)

#### ROLE OF TEA FERMENTATION

**Oxidation of Tea Flavanols (I-IV).** The withered tea leaf material is broken up in machines which cause considerable damage to the tissues involved. This action initiates a process called tea fermentation by causing the tea flavanols to come into contact with endogenous tea catechol oxidase enzymes. The tea flavanols and the tea catechol oxidase are spatially separated in the tea leaf tissues (Chalamberidze *et al.*, 1969; Tambiah *et al.*, 1966; Wickremasinghe *et al.*, 1967) so the increase in cell membrane permeability which occurs during the withering process is important in allowing the substrates and enzymes of tea fermentation to be brought together during the leaf maceration process.

Tea fermentation normally takes from 1 to 4 hr. The primary reactions taking place during this time involve the oxidative transformation of the tea flavanols (I-IV) mediated by tea catechol oxidase (Roberts, 1962; Sanderson, 1972a); this reaction is outlined in Figure 3. The tea flavanols usually constitute 15-25% of the dry weight of the tea leaf tissues, and they are transformed to colored compounds named theaflavins (IX-XII) and thearubigins

(Roberts, 1962) which give black tea its characteristic color and contribute to its taste; these reactions are outlined in Figure 4.

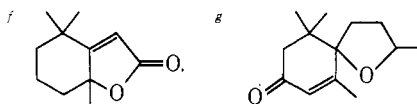
While no tea aroma constituents appear to be formed directly from the tea flavanols, the evidence does suggest that the oxidation of the tea flavanols is essential to the formation of black tea aroma. Saijo and Kuwabara (1967) have shown that holding macerated tea leaf under anaerobic conditions effectively prevents both oxidation of the tea flavanols and the formation of black tea aroma. Further, as shown in the discussion which follows, most of the known black tea aroma-forming reactions are dependent on the tea catechol oxidase-mediated oxidation of the tea flavanols.

**Transformation of Amino Acids.** Bokuchava and Popov (1954) were probably the first to show that amino acids could be converted to volatile compounds when reacted with other tea leaf constituents. These workers showed that amino acids gave rise to distinctive aromas when refluxed with "tea tannins"; *i.e.*, mixtures of black tea polyphenolic compounds. Subsequently, Popov (1956) and Skobeleva and Popov (1962) established that individ-

Table III. Black Tea Aroma Constituents Supposed to be Derived from Carotenoid Compounds<sup>a</sup>

Carotenes found in tea leaves	Primary oxidation products	Secondary oxidation products
$\beta$ -Carotene <sup>b,c</sup>	$\beta$ -Ionone + TAK <sup>d</sup>	Dihydroactinidiolide <sup>e,f</sup> 2,2,6-Trimethylcyclohexanone 5,6-Epoxyionone 2,2,6-Trimethyl-6-hydroxycyclohexanone Theaspiron <sup>e,g</sup>
$\alpha$ -Carotene <sup>b</sup>	$\beta$ -Ionone + $\alpha$ -Ionone + TAK	Theaspiron <sup>g</sup>
Xanthophyll <sup>b,c</sup>	[3-Hydroxy- $\beta$ -ionone] + [3-Hydroxy- $\alpha$ -ionone] + TAK	Theaspiron <sup>g</sup>
Neoxanthin <sup>c</sup>	[3-Hydroxy-5,6-epoxyionone] + [3,5-Dihydroxy-4,5-dihydro-6,7-didehydro- $\alpha$ -ionone] + TAK	
Phytoene <sup>b</sup>	Linalool + TAK	
Phytofluene <sup>b</sup>	Linalool + TAK	
Lycopene <sup>b</sup>	Linalool + TAK	
$\gamma$ -Carotene <sup>b</sup>	$\beta$ -Ionone + TAK	Theaspiron <sup>g</sup>
Cryptoxanthin <sup>b</sup>	$\beta$ -Ionone + [3-Hydroxy- $\beta$ -ionone] + TAK	Theaspiron <sup>g</sup>
Violaxanthin <sup>b,c</sup>	[3-Hydroxy-5,6-epoxyionone] + TAK	
Zeaxanthin <sup>b</sup>	[3-Hydroxy- $\beta$ -ionone] + TAK	Theaspiron <sup>g</sup>

<sup>a</sup> Adapted from Sanderson *et al.* (1971). Arrows indicate degree of certainty of reactions indicated by results of this investigation as follows: established reaction  $\longrightarrow$ ; highly probable reaction  $\dashrightarrow$ ; probable reaction  $-\cdot-\cdot-\cdot\rightarrow$ . Compounds shown in brackets have not yet been identified in tea. <sup>b</sup> Tentatively identified by Tirimanna and Wickremasinghe (1965). <sup>c</sup> Identified by Nikolaishvili and Adeishvili (1966) and by Sanderson *et al.* (1971). <sup>d</sup> TAK = terpenoid-like aldehydes and ketones; oxidation products of all carotenes listed. <sup>e</sup> Kawashima and Yamanishi (1973) have found that dihydroactinidiolide<sup>f</sup> and theaspiron<sup>g</sup> are formed on heating  $\beta$ -carotene.



ual amino acids gave rise to CO<sub>2</sub>, NH<sub>3</sub>, and corresponding decarboxylated and deaminated aldehydes under these conditions. These results and the results of the corroborating work of Nakabayashi (1958a,b,c) are summarized in Table II.

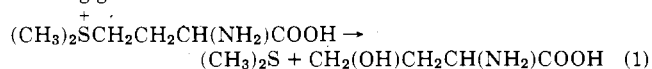
More recently, Saijo and Takeo (1970a,b) and Co and Sanderson (1970) used <sup>14</sup>C-labeled amino acids and model tea fermentation systems to show that the  $\alpha$ -amino acids present in tea leaf material will undergo Strecker degradation to form corresponding aldehydes in the presence of, and only in the presence of, oxidizing tea flavanols. These results are summarized in Table II and Figure 5. It is known (see review by Reynolds, 1970) that virtually any  $\alpha$ -dicarbonyl compound can bring about the Strecker degradation of  $\alpha$ -amino acids, and it is presumed that the *ortho*-quinones (V-VIII) formed from the tea flavanols (I-IV) during tea fermentation (Figure 3) act as the driving force for these reactions during conversion of fresh green tea leaf to black tea.

It was found (Co and Sanderson, 1970) that some  $\alpha$ -amino acids did not give rise to volatile aldehydes in the tea fermentation system (Table II), and it was recognized that this result might be due to the formation of nonvolatile products. Subsequent work has shown (Moss *et al.*,

1972) that [<sup>14</sup>C]glutamic acid is converted, in part, to the relatively nonvolatile substance [<sup>14</sup>C]succinimide in the tea fermentation system, and so it seems likely that all of the  $\alpha$ -amino acids present in tea leaf are converted to some extent to Strecker degradation products which may be either volatile or nonvolatile.

As to the importance of the aldehydes derived from amino acids in determining the flavor of black tea, they must have some impact on the overall flavor impression inasmuch as these aldehydes are odiferous substances. However, it is known (Dukker *et al.*, 1972) that none of these aldehydes, or any combination of them, is even faintly tea-like by itself.

The possibility that other types of aroma constituents are formed from amino acids is shown by results obtained by Kiribuchi and Yamanishi (1963). These investigators identified methylmethionine sulfonium salt in green tea extracts and found evidence that this compound was converted, in part, to dimethyl sulfide and homoserine on heating green tea in water.



Dimethyl sulfide is a component of black tea aroma

(Bondarovich *et al.*, 1967; Wickremasinghe and Swain, 1965), so it appears likely that the results obtained by Kiribuchi and Yamanishi (1963) have importance in the formation of black tea aroma.

It is noteworthy that Finot *et al.* (1967) have shown that some phenylacetaldehyde is formed from phenylalanine under conditions which approximate a tea drinker's usual tea brewing procedure. These results suggest that the tea brewing procedure itself may be important in the formation of black tea flavor, but this possibility is as yet virtually untested.

**Transformation of Carotenes.** Early work by Roberts (1958) indicated that the amount of the carotenes present in fresh tea leaves was greater than in black tea. In a more recent study of tea carotenes, Tirimanna and Wickremasinghe (1965) tentatively identified nine carotenoid compounds (four more suspected carotenes were unidentified) in fresh tea leaf (Table III), and they confirmed that the amount of these compounds decreased at each step of the black tea manufacturing process. Tirimanna and Wickremasinghe (1965) hypothesized at this time that the carotenes might well be undergoing changes to black tea aroma constituents. Nikolaishvili and Adeishvili (1966) and Sanderson *et al.* (1971) confirmed the loss of carotenes during black tea manufacture in investigations which included quantitative determinations of the carotenes, but these investigators only reported the presence of four carotenoid compounds in tea leaf tissues (Table III).

Meanwhile, Müggler-Chavan *et al.* (1966, 1969) and Bricout *et al.* (1967) identified  $\beta$ -ionone and some derivatives of  $\beta$ -ionone (Table III) in black tea aroma, and they suggested that these compounds may have originated from the oxidative degradation of carotenes during black tea manufacture.

The speculations of Tirimanna and Wickremasinghe (1965) and of Müggler-Chavan *et al.* (1966, 1969) and Bricout *et al.* (1967) were substantiated when Sanderson *et al.* (1971) demonstrated that  $\beta$ -carotene was converted to  $\beta$ -ionone and several other unidentified compounds during tea fermentation. These results are summarized in Table III. The formation of  $\beta$ -ionone from  $\beta$ -carotene took place readily in fermenting tea leaf under normal black tea manufacturing conditions; *i.e.*, at room temperature in macerated tea leaf material at about 60% moisture content. However, in the model tea fermentation system,  $\beta$ -carotene underwent no appreciable change until *both* of the following conditions had been met: tea flavanol oxidation had taken place, and the model system had been taken to dryness on a steam bath. There was no appreciable change in  $\beta$ -carotene in either tea leaf or in the model tea fermentation system when the tea enzymes were inactivated prior to introducing  $\beta$ -carotene to the system. These results suggest that oxidized tea flavanols formed during tea fermentation (Figure 3) are the oxidizing agents which cause the oxidative degradation of carotenes present in tea leaf, but that the oxidation potential must be raised to a critical level (*i.e.*, by concentrating the reactants in the tea fermentation system, or by heating, or both) before these changes can take place. These results are summarized in Figure 6.

The volatile compounds formed from carotenes during the manufacture of black tea (Table III) have strong flavor impressions, which suggests that they must be important in determining the character of black tea aroma. This fact, together with the fact that the oxidation potential required to effect the oxidative degradation of carotenes is critical in the black tea manufacturing system, suggests that these reactions are important in explaining why manufacturing conditions do have an important effect on the flavor of finished black tea products.

**Transformation of Linolenic Acid.** The major free

fatty acid present in tea leaf is linolenic acid (Dukker, 1972). The possibility that this polyunsaturated fatty acid would undergo oxidative degradation during tea fermentation was investigated by Gonzalez *et al.* (1972a). The results of this investigation showed that *trans*-2-[ $^{14}$ C]hexanal was formed from [ $^{14}$ C]linolenic acid in fermenting tea leaf and that the quantity of *trans*-2-[ $^{14}$ C]hexanal was increased when the fermented tea leaf was fired. Again, inactivation of the tea leaf enzymes prior to addition of the [ $^{14}$ C]linolenic acid prevented the formation of any labeled volatiles. The surprise in this investigation was that only one volatile compound was formed. If other products were formed, they were nonvolatile, and they would not have been detected by the procedures used.

#### ROLE OF FIRING

The role of firing in black tea aroma formation is very poorly understood at the present simply because it has received little attention from researchers. However, the fact that it is important is readily apparent when one tastes samples of tea leaf materials at strategic points in the black tea manufacturing process (Bokuchava *et al.*, 1957; Gonzalez *et al.*, 1972b). Under favorable conditions (*i.e.*, good quality tea leaf, good location, good tea factory, good weather, and good manufacturing procedures) the fermented but unfired tea leaf material will produce a tea infusion with a distinctly flowery, greenish aroma. After firing, this same tea leaf material, now properly called black tea, will produce a tea infusion which is readily recognized as being flavory and black tea-like.

The firing operation normally takes about 20 min, during which time the moisture content of the tea leaf material is reduced from about 60 to about 3%, and the leaf temperature rises rapidly from room temperature (about 22°) to about 65° and then steadily to about 85°. During this time, it is likely that the enzymic processes taking place during tea fermentation will continue at an accelerated pace until the enzymes are finally inactivated by the heat. It seems likely that the oxidizing agents which are formed (Figure 3) under these conditions, *i.e.*, relatively high temperatures and increasing concentration of reactants, may give rise to unusually high oxidation potentials. This may explain how the driving force is developed for some flavor-forming reactions which only take place on firing.

It has been found (Gonzalez *et al.*, 1972b; Yamanishi *et al.*, 1966) that firing causes a general loss of aroma constituents. Yamanishi *et al.* (1966) have carried out a detailed study of this process, and they found that there are appreciable losses in virtually all the alcohols, carbonyls, and phenolic compounds present in fermented tea leaf when this material is fired. At the same time it was found that there are significant increases (*i.e.*, relative to other tea aroma constituents) in the amounts of the aliphatic carboxylic acids present, which suggests that some oxidations are taking place during this treatment. The suggestion (Eyton, 1972) that the adjustment of the relative amounts of aroma constituents which takes place during the firing process may be important in determining the character of black tea aroma is most reasonable, but it has yet to be verified.

Recently, Kawashima and Yamanishi (1973) have shown that ten volatile compounds were formed on heating  $\beta$ -carotene. The compounds identified included  $\beta$ -ionone and dihydroactinidiolide. The latter compound is reported (Ina *et al.*, 1968; Sakato and Ina, 1970; Sakato *et al.*, 1972) to be an important black tea aroma constituent. Sakato and Ina (1972) report that dihydroactinidiolide (see Table III, footnote *f*) has a weak black tea aroma itself and that its black tea impression is enhanced by the copresence of theaspironone (see Table III, footnote *g*). The likelihood that these reactions (Table III) take place dur-

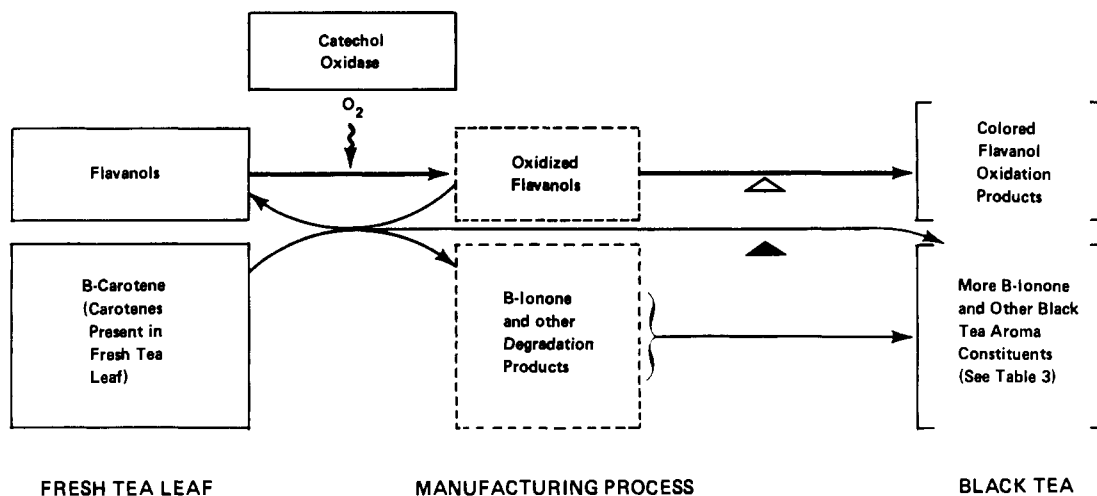


Figure 6. Scheme showing formation of volatile compounds from carotenes during tea fermentation.  $\Delta$ , transformations resulting from enzymic oxidations and firing.  $\blacktriangle$ , transformations resulting from firing. (Adapted from Sanderson *et al.*, 1971.)

ing the firing stage of the black tea manufacturing process suggests that much important information on black tea aroma formation awaits the investigators who study the chemistry of the firing process.

#### EFFECT OF ENVIRONMENTAL FACTORS

It is known (Keegel, 1958; Sanderson, 1964b) that environmental factors surrounding the black tea manufacturing process do affect the flavor of the finished product. There is little specific information on the chemistry of these effects, but temperature must affect the outcome of the tea conversion process by affecting the time required and the relative rates of the several reactions taking place, and humidity must affect the uniformity of the tea conversion process within the tissues by affecting the uniformity of moisture content of the tea leaf material involved. Isoe *et al.* (1969) report that  $\beta$ -ionone and dihydroactinidiolide are formed when  $\beta$ -carotene is irradiated with uv light, suggesting that the lighting conditions within tea factories are also important in determining the flavor of the finished product.

#### BIOSYNTHETIC REACTIONS

In contrast to the reactions described above in which black tea aroma constituents are formed by the oxidative degradation of nonvolatile precursors brought about by oxidizing agents formed enzymically in the tea fermentation process (Figure 3), there is some evidence that biosynthetic reactions are important in the black tea aroma-forming process. Wickremasinghe and his coworkers (Wickremasinghe, 1967; Wickremasinghe and Sivapalan, 1966; Wickremasinghe and Swain, 1964, 1965; Wickremasinghe *et al.*, 1969) have been the principal workers in this area.

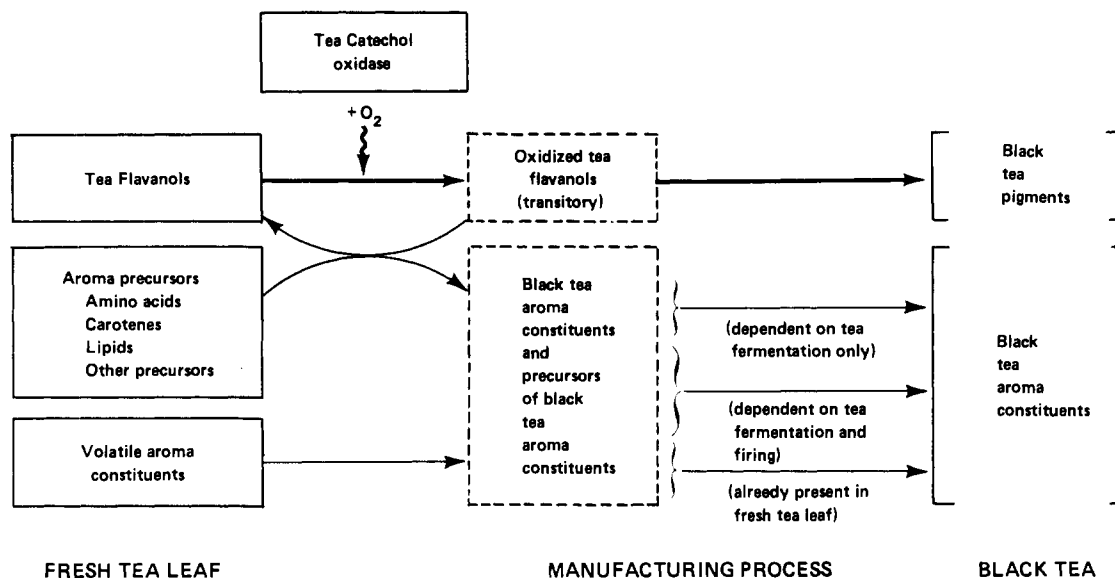
The finding that the level of the amino acid *L*-leucine was lower in flavory black teas than in nonflavory black tea (Wickremasinghe and Swain, 1965) led Wickremasinghe (1967) to suggest that *L*-leucine might be one of the precursors of some of the compounds contributing to black tea flavor. Wickremasinghe and Sivapalan (1966) showed that [<sup>14</sup>C]-*L*-leucine and [<sup>14</sup>C]acetate are transformed *via* mevalonic acid to three volatile compounds and carotenes, in detached metabolizing tea flush. The volatile compounds are unidentified, but they give terpene color reactions with anisaldehyde-H<sub>2</sub>SO<sub>4</sub> reagent (Wickremasinghe, 1972). In another investigation, Saijo and Uritani (1971) have shown that 2-[<sup>14</sup>C]acetate is converted into nerolidol in excised tea shoots but not into either linalool, nerol, geraniol, or farnesol.

Further investigation identified other biochemical factors in fresh tea flush which are presumably needed for the formation of terpenes (Cornforth, 1968; Loomis, 1967). Specifically, Wickremasinghe *et al.* (1969) detected the enzyme transaminase and the cofactors Coenzyme A, manganese, and iron in fresh tea flush; and Selvendran (1969) investigated the metabolism of nucleotides and phosphate esters in tea leaf material during black tea manufacture.

While the role of biosynthetic reactions in forming black tea aroma constituents is only poorly defined as yet, these reactions must be important in at least three ways. First, the volatiles present in fresh tea flush must be formed biosynthetically and some of these compounds remain in the tea leaf material throughout the black tea manufacturing process to form a portion of the black tea aroma complex. Second, the precursors of the black tea aroma constituents which are formed during the black tea manufacturing process must be formed biosynthetically, and many of the precursors are formed by biosynthetic mechanisms requiring the enzymes and cofactors identified in tea leaf material by Wickremasinghe and Sivapalan (1966), Wickremasinghe *et al.* (1969), and Selvendran (1969). Third, some biosynthetic activity may go on in tea leaf material during the black tea manufacturing process, and the results of Wickremasinghe and Sivapalan (1966) suggest that this is the case.

#### SUMMARY

The available information relating to the formation of black tea aroma is discussed in the preceding sections of this paper. Our interpretation of this information is summarized in Figure 7. In brief, the existing experimental evidence suggests that black tea aroma formation is dependent on the oxidation of tea flavanols during a stage of black tea manufacture called tea fermentation and a subsequent firing step. The oxidized tea flavanols act indiscriminately on other susceptible constituents of the tea leaf tissue involved such as amino acids, carotenes, unsaturated fatty acids, etc., causing them to be oxidatively degraded. Further, a firing step following the tea fermentation step has been found to be required for the formation of black tea aroma. The chemistry of the firing step as it is known today is similar to that of the tea fermentation process, but the possibility remains that aroma-forming reactions which are peculiar to firing will be discovered in future investigations. In any case, when the products of the reactions occurring during tea fermenta-



**Figure 7.** Proposed scheme for formation of black tea aroma. Materials present in fresh (withered) tea flush are enclosed in rectangles. Materials present in dashed enclosures are largely transitory in that they are undergoing change during the black tea manufacturing process. Materials present in brackets are those present in the finished black tea product. The amount of any of the above materials present in the black tea produced would be dependent on the conditions of manufacture.<sup>a</sup>

**Table IV. Classes of Flavor-Forming Mechanisms in Food Systems**

Class	Description	Examples
I. Biosynthetic	Flavor constituents formed directly by biosynthetic processes.	Flavors based on terpenoid and ester compounds such as mint, <sup>a</sup> citrus, <sup>b</sup> muskmelon, <sup>c</sup> pepper, <sup>d</sup> banana, <sup>e</sup> etc.
II. Direct enzymic	Flavor constituents formed by enzymes acting on specific flavor precursors.	Formation of onion flavor <sup>f</sup> by action of alliinase on sulfoxides; cabbage <sup>f</sup>
III. Oxidative (indirect enzymic)	Flavor constituents formed by oxidation of flavor precursors by enzymically-formed oxidizing agents.	Flavors characterized by presence of carbonyl and acid compounds such as tea <sup>g</sup> (see text for additional details)
IV. Pyrolytic	Flavor constituents formed from precursors by a heating or baking treatment.	Flavors characterized by presence of pyrazines (coffee, <sup>h,i</sup> chocolate, <sup>h,j</sup> etc.), furans (bread <sup>h,k</sup> ), etc.

<sup>a</sup> Smith and Levi (1961). <sup>b</sup> Kefford and Chandler (1970). <sup>c</sup> Kemp *et al.* (1972). <sup>d</sup> Haymon and Aurand (1971). <sup>e</sup> Tressl *et al.* (1970). <sup>f</sup> Schwimmer and Friedman (1972). <sup>g</sup> Sanderson (1972a); this paper. <sup>h</sup> Reynolds (1970). <sup>i</sup> Gautschi *et al.* (1967); Friedel *et al.* (1971). <sup>j</sup> Marion *et al.* (1967); Flament *et al.* (1967); Rizzi (1967); van Praag *et al.* (1968). <sup>k</sup> Fagerson (1969).

tation and firing are volatile, they form part of the black tea aroma complex.

Biosynthetic reactions are most important in that they determine the composition of the raw material of black tea manufacture, namely the fresh green tea flush. Some of these reactions lead to the formation of volatile compounds in the tea flush which are carried over into the finished black tea, and there is evidence that some of these biosynthetic reactions continue to take place during tea fermentation (Wickremasinghe and Sivapalan, 1966). These reactions must play some part in determining the character of black tea aroma (Figure 7), but the fact that tea fermentation and firing are essential to black tea aroma formation makes it clear that these biosynthetic reactions are only contributory. Certainly, biosynthetic reactions are essential to the formation of black tea aroma precursors.

It is clear from the evidence available that the aroma-forming reactions which take place during black tea manufacture as a result of tea fermentation and firing involve many different precursors, oxidizing agents, and products.

Further, the relative amount of any one of the reactions taking place must depend on the usual thermodynamic factors such as concentration of reactants (affected by composition of tea leaf material, activity of catechol oxidase, water content of tea leaf material, degree of homogenization of tea leaf constituents achieved in leaf maceration step, etc.), relative oxidation potentials of reactants (affected by concentration of reactants, pH and temperature of tea leaf tissues, activity of catechol oxidase, etc.), and length of time allowed for the various processes to take place. Realization of the myriad of reactions taking place in the black tea aroma-forming process and the multiplicity of factors affecting these reactions brings a realization that it will be difficult to predict the ideal composition of tea flush or the best possible manufacturing conditions required to produce a black tea with the best possible aroma. This realization does, however, make it easy to understand that the composition of the tea flush and the manufacturing conditions do have an effect on the aroma of the finished black tea product. In fact, similar arguments can be constructed to show that these factors



are important in determining all of the organoleptic properties of black tea (Sanderson, 1965, 1972a).

The question as to whether the peculiar character of black tea flavor is determined by one or more specific compounds formed during the manufacture of black tea or whether it is due to the particular balance of aroma constituents which results from the black tea manufacturing process is unanswered. Ina *et al.* (1968) have reported that dihydroactinidiolide and theaspironone contribute significantly to the aroma of black tea, but attempts in our laboratory (Dukker *et al.*, 1972) to duplicate these results have not been successful. However, it is also known that many black tea aroma constituents are as yet unidentified. The fact that different black teas have such different relative amounts of the several aroma constituents (Yamanishi *et al.*, 1968a,b), even though the flavor of virtually all black teas is readily recognized as black tea, appears to argue against the relative amount of the tea aroma constituents being the factor which determines black tea character. Of course, even if the balance of aroma constituents does not determine the basic black tea flavor, this balance must be most important in modifying this flavor to produce the distinctive, and the not so distinctive, teas of the world.

In conclusion we suggest that the evidence available to date indicates that black tea aroma formation (Figure 7) is primarily due to oxidation of flavor precursors by oxidizing agents formed enzymically during the tea fermentation process (Figure 3). This mechanism for aroma formation is called Class III in Table IV, where a summary of flavor-forming mechanisms in food systems is proposed. In fact, tea, as well as virtually every other food, can only be classified by its predominant flavor-forming mechanism, since examples of all classes of mechanisms may be found to be part of the black tea aroma-forming mechanism.

Further development of our knowledge of the chemistry of black tea aroma formation should be invaluable in applications such as: selection of clones of tea plants; designing black tea manufacturing processes for specific purposes (*i.e.*, for use with special clones chosen for particular properties) and to produce black tea products with desired flavor characteristics; and development of improved instant tea manufacturing processes, especially those which use fresh green tea flush as starting material (Pintauro, 1970; Sanderson, 1972b). We look to future developments in this area of tea chemistry with anticipation.

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## Structure-Activity Correlations in DDT Analogs

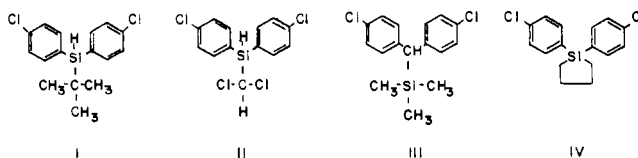
Mohamed A. H. Fahmy, T. Roy Fukuto,\* Robert L. Metcalf,<sup>1</sup> and Roy L. Holmstead<sup>2</sup>

The relationship between the structure of a series of DDT analogs and the insecticidal activity to houseflies and mosquito larvae was examined by means of multiple regression analysis using the substituent constants  $E_s$ ,  $\pi$ ,  $\sigma^*$ ,  $F$ , and  $R$ . The

steric substituent constant  $E_s$  was the single most important parameter for the correlation of insecticidal activity when substituents are varied on the aromatic ring and on the  $\alpha$ -carbon atom.

In connection with our continuing efforts to discover new approaches for the design of selective and biodegradable insecticides, the synthesis and evaluation of the insecticidal activity of a series of silicon-containing analogs of DDT were carried out. The structures of some of these compounds in which silicon occupies a key position in the molecule are given below. The rationale behind the

examination of silicon DDT analogs as biodegradable insecticides resides in the greater instability of the C-Si bond compared to the C-C bond to ionic and radical reactions.



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To our disappointment, virtually all of the approximately 20 silicon analogs, including I-IV, were ineffective against houseflies, showing little or no toxicity at 500  $\mu\text{g/g}$ , alone or in combination with the synergist piperonyl