

Various Interactions in Chocolate Flavor^{1,2}

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ABSTRACT

More than 300 volatile compounds have been identified in roasted cocoa beans and its products, making chocolate one of the most complicated natural flavors. Most beans, after harvesting, are subjected to a fermentation that is an important step in the formation of flavor precursors. Roasting is essential to the development of chocolate flavor both with respect to the loss of undesirable volatiles and the generating of key aroma compounds. Flavor is modified to meet demand using blends of beans and through variation in roasting conditions and the mechanical treatments employed to process beans into chocolate liquor and coating. The effect of fermentation and roasting on certain chemical properties related to flavor in chocolate is reviewed. Particular attention is given to monocarbonyls, head-space volatiles, pyrrole aldehydes and alkylypyrazines.

INTRODUCTION

Flavor in chocolate is influenced by many variables including the type of beans used, postharvest treatments involved in preparing the crop for export from tropical, producing countries, and processing in the chocolate factory. This presentation concentrates primarily on two of the more important flavor events between the cocoa tree and finished chocolate confections, namely fermentation and roasting. It is not intended as a review of all pertinent findings about the flavor of chocolate. Research conducted in the author's laboratory is emphasized, with appropriate reference to the findings of other scientists that fit this particular discussion of chocolate flavor.

By the early 1960's only a few chocolate volatiles had been identified. Now the list includes more than 300 compounds (Tables I and II), all of which are found in cocoa beans after roasting. Differences among samples are quantitative, not qualitative; at least no one has to this time proven otherwise. For specific information about the compounds contributing to Tables I and II, the following references should be consulted (1-24).

Cocoa beans vary somewhat in size and shape with 1 g being a representative weight. Beans, before roasting, taste astringent, bitter, acidy, musty, unclean, nutty or even chocolate-like depending on the particular batch examined. Unroasted beans ground in a blender will have an aroma reminiscent of corn or grass silage. Chocolate manufacturers use terms such as low roast, medium roast and high roast, with factors such as type of bean and their ultimate use governing temperature and roasting times.

Bean Roasting

During roasting, beans take on the more typical aroma of processed chocolate products. This involves more than just the generation of new volatile material through pyrolysis of sugars and nitrogenous substances. The aroma in the early stages of a roast may be like vinegar, may be reminiscent of a brewery or bakery, or it may be something

else. Loss of these "low boilers" indigenous to raw beans undoubtedly has an important bearing on the final flavor quality of chocolate.

The development and modification of flavor is not the only reason for roasting cocoa beans. During roasting, the pressures from escaping internal gases, including water vapor, disrupt cellular structures, make the bean more brittle, and cause loss of the adhesive-like quality of the hull. The hull can then be separated easily from the more dense nib in the cracking and winnowing machine. Also, roasting obviously greatly reduces the microbial population (25).

Another key event during roasting is the reduction in moisture content from 6% to ca. 1%. Quite likely, the initial and final water content, and its rate of removal from the beans, influence the direction of heat-induced reactions and thereby affect the flavor-developing process.

Further Processing

Following roasting and removal of hulls and "fines," the nibs are pulverized in grinding mills to particle sizes not detectable to the palate. Much mechanical energy is absorbed, and cocoa fat melts to become the continuous phase with the nonfat portion embedded in it. Surface exposures during grinding and the rise in temperature caused by shearing would be expected to influence the concentration of the more volatile components in the liquor.

Further processing of chocolate liquor quite often involves temperatures that could initiate flavor change. As an example, 150 C may be reached during hydraulic pressing to recover cocoa butter and cocoa cake.

In the manufacture of chocolate coatings, a mix of liquor, cocoa butter and sugar, with or without milk solids, is passed through roller refiners to reduce the size of sugar crystals and coat them with lipid. Even though the rollers are water-cooled to prevent overheating of the paste, refining has a pronounced effect on flavor. Considering the thin film of chocolate on the rollers and the great increase in chocolate surfaces, a weeding out and redistribution of flavor components can be visualized.

The final step in the manufacture of chocolate is conching, a process to which all good chocolates are subject. Conching may involve the mixing or rolling of the chocolate mass for periods as long as 3 days at temperatures between 50 C and 80 C.

Conching has a remarkable mellowing effect on the flavor of chocolate. Unfortunately, published research on this important process is quite meager, and any explanation of why flavor is modified must be termed speculative. Aeration which allows the escape of undesirable volatiles, oxidative changes and even Maillard browning have been implicated. Since conching is primarily a mechanical process, changes related to surface phenomena must be of great importance.

TABLE I

Compounds Identified in Studies of Chocolate Aroma	
Compound	Number
Aliphatic	141
Aromatic, heterocyclic	143
Terpenoids	22
Total	306

¹One of 13 papers presented in the symposium "Flavor Research in Fats and Fat Bearing Foods," AOCs Meeting, Atlantic City, October 1971. Presented in part in the symposium "Thermally Produced Flavor Components," American Chemical Society Meeting, Washington, D.C., September 1971.

²Paper No. 4135 in the Journal Series of the Pennsylvania Agricultural Experiment Station.

TABLE II

Classes of Compounds Identified in Studies of Chocolate Aroma

Class	Number	Class	Number
Hydrocarbons	34	Ketones	30
Alcohols	30	Furans	15
Acids	37	Amines	8
Esters	54	Nitrile	3
Ethers, acetals	11	Pyrroles	10
Lactones	5	Pyrazines	31
Aldehydes	25	Sulfur	13

Harvesting and Fermenting

Actually the flavor developed in the chocolate factory is very dependent upon what happens to the beans at their point of origin.

Depending on genetic stock and growing conditions, pods from various parts of the world may vary in shape, size and color, and in the size, color and number of beans contained therein. Chocolate experts can detect flavor differences related to geographic origin, variety and agronomic practices.

However it is also widely accepted that postharvest events are of critical importance to the development of good chocolate flavor when the beans finally get to the chocolate factory and are roasted. This encompasses the things that happen after the ripe pods are cut from the tree and opened to expose the beans to the elements until they are dried to a safe, storable moisture level of 5-8%. The moisture level in beans is ca. 35% when removed from the sterile pod, and, depending on treatments, it will take from 3-10 days or more to get them to the dried state; this is in the hot and humid tropics where man cannot master his environment nearly as well as in more temperate regions. Considering the environmental uncertainties with which the grower must contend, the degree of standardization achieved is quite remarkable.

In most regions of production, cocoa beans are allowed to ferment, a process which favors the formation of flavor precursors. Fermentation practices differ among and within geographic regions; the process may last 3 days or 7 days, and may take place in sweat boxes, barrels, bins, trays, a hole in the ground or a bundle of banana leaves.

Early in the fermentation process, yeasts convert the glucose of the pulp into alcohol which is then oxidized to acetic acid. Some evidence suggests that lactic acid accumulates, and its presence, especially at high levels, is a characteristic of well fermented beans (22). During fermentation the bean mass may reach temperatures as high as 50 C (26). The combination of heat and acid kills the bean; thus germination is prevented and cellular membranes within the bean are altered.

Chemical changes taking place within the bean during fermentation represent a fascinating and most important subject for study. Reviews of progress dealing with the chemistry of fermentation have been authored by Rohen (26), Roelofsen (27), and Forsyth and Quesnel (28). Membrane changes appear to be a key segment in the sequence of reaction leading to the development of flavor precursors. Enzyme-substrate contact is realized, sucrose and protein are hydrolyzed, and polyphenolic material is oxidized. Complexes are formed that both figuratively and literally are very complex and poorly understood. A leaching out of the alkaloids and other soluble constituents occurs to a certain extent (26).

We can assume that two concurrent fermentations are taking place, one within the bean and the other outside in the pulp. During fermentation the beans swell, suggesting the passage of some products of microbial metabolism into the bean. What is absorbed from the pulp and how chocolate flavor is affected by this phenomenon need to be elucidated.

Headspace Volatiles

Free amino acids, reducing sugars and their degradation products constitute a pool of precursors for many of the classical thermally initiated reactions that lead to changes in flavor and color. Bailey et al. (1) were the first investigators to suggest and provide evidence that the Strecker reaction was an important occurrence during roasting. Gas liquid chromatography-mass spectrometry (GLC-MS) headspace analysis of beans revealed isobutyraldehyde and isovaleraldehyde as headspace components that develop during roasting.

Following Bailey, several groups used the headspace approach to study various aspects of cocoa (29-31). Figure 1 (headspace analysis) shows the effect of roasting temperature on the generation of isobutyraldehyde and isovaleraldehyde through the Strecker reaction. In general the potential for generating Strecker aldehydes during roasting will be greatest in beans from countries where efforts are made to ferment the crop. In view of the considerable amount of proteolysis taking place during fermentation, the correlation found is a logical one. Protein breakdown accelerates when the bean dies after ca. 48 hr, and membranes are altered to allow enzyme-substrate contact (28).

Isovaleraldehyde, arising from leucine, is most certainly present in chocolate at a concentration sufficient to influence flavor. Grind-roasted cocoa beans and the aroma of isovaleraldehyde will be readily discerned. While the Strecker aldehydes are themselves important components of chocolate flavor, more is involved. One of the compounds isolated by van Praag et al. (13) was 5-methyl-2-phenyl-2-hexenal. Of the more than 300 compounds identified to date, this one comes closest to being unmistakably chocolate-like in aroma, and van Praag speculated that this important component of chocolate aroma could very well be a "dehydrated aldo condensation" product between phenylacetaldehyde and isovaleraldehyde. Phenylacetaldehyde logically comes from phenylalanine via the Strecker reaction. Interestingly our data (32) show that the two most abundant free amino acids in cocoa beans are leucine and phenylalanine.

Monocarbonyls

Another indication of change attributable to roasting is presented in Table III which summarizes data on monocarbonyls collected early in our chocolate research program (3). Results can vary considerably, but the trends shown are fairly representative of that found for most samples. Roasting usually resulted in increases in concentrations for the saturated and unsaturated aldehydes, whereas methyl ketones decreased.

Aromas emitted when the carbonyl fractions were regenerated from the hydrazones were: methyl ketone, cheesy; saturated aldehyde, waxy and fruity; 2-enal, advanced oxidized and painty; 2,4-dienal, spicy and nutmeg. None were chocolate-like either by themselves or in combination. However quantitative data indicated that the saturated aldehydes, 2-enals and 2,4-dienals were present at concentrations sufficient to influence the character of chocolate flavor.

TBA Reaction

When cocoa beans are pulverized in water, then reacted with thiobarbituric acid (TBA) for a few minutes, a yellow pigment is formed which has a well resolved absorption maximum at 437 m μ (33). No pigment is formed when raw beans are subjected to the test. Only roasted beans react, and the absorption at 437 m μ correlates nicely with thermal input.

Figure 2 shows the development of the TBA reactant as a function of roasting time at constant temperature. Within

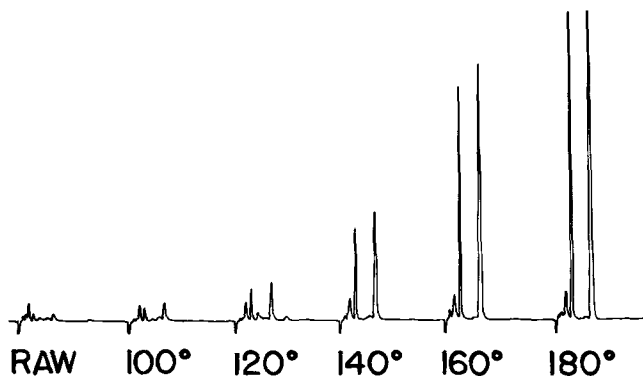


FIG. 1. Composite chromatograms of headspace volatiles from gas liquid chromatographic analyses of cocoa beans roasted for 30 min at various temperatures.

the range of temperatures and times common to the roasting of cocoa beans, the curve is linear, but extended roasting results in the complete consumption of the precursor of the thermally produced TBA reactant. Primarily through thin layer chromatography we discovered that the principal reactant was formyl-2-pyrrole or pyrrole carboxaldehyde (PCA) which has been identified as a constituent of chocolate (10). Approximately 40% of the TBA reacting potential is contributed by PCA.

Literature dealing with the pyrrole aspect of browning is quite limited. Kato's (34) scheme for N-substituted pyrrole aldehydes should yield PCA through reaction of a pentose and ammonia. While the ammonia content of fermented cocoa beans is relatively high and contributes almost as much nitrogen as all of the free amino acids combined, we have not been able to find any pentose in the nib fraction of cocoa. A clue concerning the origin of PCA is that, when the hulls are laboriously peeled from raw cocoa beans and then roasted, extremely high TBA values are obtained for this material.

The relative simplicity of the TBA method suggests its use in research and as a routine quality control test for monitoring the variables associated with the roasting of cocoa beans. A somewhat similar procedure has been used to follow the cooking of milk caramel confections (35), and recent work in our laboratory indicates that it can be applied to peanuts and other oil or dry roasting nut products. Since ethyl and methyl vanillin also form a yellow pigment with TBA, caution must be exercised when applying the test to food systems which might contain these flavor additives.

Alkylpyrazines

Accompanying the refinement of GLC-MS techniques for the characterization of food volatiles, alkylpyrazines were discovered as an important class of compounds contributing to flavor in many food products, especially those subjected to a roasting process. One of the earliest references was Dietrich et al. (4) who found 2,6-dimethylpyrazines in chocolate. To date more than 30 alkylpyrazines have been identified in roasted cocoa beans and products made therefrom.

Figure 3 shows a chromatogram of the major methyl- and ethyl-substituted pyrazines in roasted cocoa beans (32). Except for peaks 2 and 3 they appear to be single components, at least as determined by GLC-MS. They are as follows: (1) pyrazine internal standard; (2) acetoin and methylpyrazine; (3) 2,5- and 2,6-dimethylpyrazine and 2-ethylpyrazine; (4) 2,3-dimethylpyrazine; (5) probably 2-ethyl-6-methylpyrazine; (6) 2-ethyl-5-methylpyrazine; (7) trimethylpyrazine; (8) 2,5-dimethyl-3-ethylpyrazine; (9) probably 2,3-dimethyl-6-ethylpyrazine; (10) tetramethylpyrazine; and (11,12) nonpyrazines.

TABLE III

Effect of Roasting on the Monocarboxyls of Cocoa Beans

Monocarboxyl	$\mu\text{Moles}/100 \text{ g fat}$	
	Raw	Liquor
Methyl ketones	16.7	11.0
Saturated aldehydes	14.0	44.0
2-Enals	1.4	2.6
2,4-Dienals	1.7	3.2

Roasting temperatures for cocoa beans may vary from 90 C to 150 C or higher. Heat transfer and thermally induced chemical change at these temperatures will of course be influenced by such factors as hold time, air movement and the design of the roaster. Consequently, care must be exercised when relating data from roasting trials in the laboratory to what happens at specific temperatures under commercial conditions. With this cautionary statement in mind, Figure 4 is presented to illustrate the effect of air temperature on the development of alkylpyrazines during roasting.

As shown in Figure 4, alkylpyrazines were formed in cocoa beans at the lowest roasting temperature (75 C) employed in the study, but temperatures of 125 C and higher were needed before the pyrazines could be generated in relatively large amounts. It is of interest to note that the most highly prized flavor beans are usually roasted at temperatures that would not yield significant quantities of alkylpyrazines. On the other hand, the basic Bahia and Ghana beans are most often roasted at temperatures above 125 C, which should result in relatively high concentrations. From this we can conclude that differences in flavor among chocolates can be attributed in part to the presence or absence of large amounts of alkylpyrazines. This statement can also be extended to include qualitative differences within alkylpyrazine fractions, since it has been demonstrated that some homologs are generated more easily than others (32).

Tetramethylpyrazine (TMP) was the only alkylpyrazine found in unroasted cocoa beans. It was present in small amounts (20 $\mu\text{g}/100 \text{ g beans}$) in most samples from countries that export well fermented beans. TMP was not detected in lightly fermented Arriba beans or in unfermented Tabasco and Sanchez beans. TMP in unroasted beans is undoubtedly of microbial origin. Ostovar (36) has shown that during the latter stages of fermentation Bacilli, including *B. subtilis*, are the dominant microorganisms present in the cocoa bean mass. Biosynthesis of TMP by *B. subtilis* in fermenting soy sauce has been demonstrated (37).

The effect of fermentation is illustrated further by Figure 5 which compares alkylpyrazine formation in Ghana and Sanchez beans as a function of roasting time at 150 C. In fermented Ghana beans the precursors were readily labile, resulting in a rapid generation of alkylpyrazines to a maximum concentration which did not change significantly upon further roasting. This is in marked contrast to unfermented Sanchez beans which yielded pyrazines at a much slower rate, and even after 90 min in the roaster the concentration had not reached the maximum level developed in the Ghana beans. As a point of reference, it is the author's opinion that under the laboratory conditions employed roasting periods longer than 30-45 min would have been excessive, since unpleasant scorched or burnt characteristics were becoming dominant.

We can assume that during roasting alkylpyrazines are generated through classical nonenzymatic browning reactions as proposed for other products such as peanuts (38). The precursor pool would include the sugars, especially reducing sugar, and the amino acids, amines and ammonia, each profoundly affected by the fermentation process.

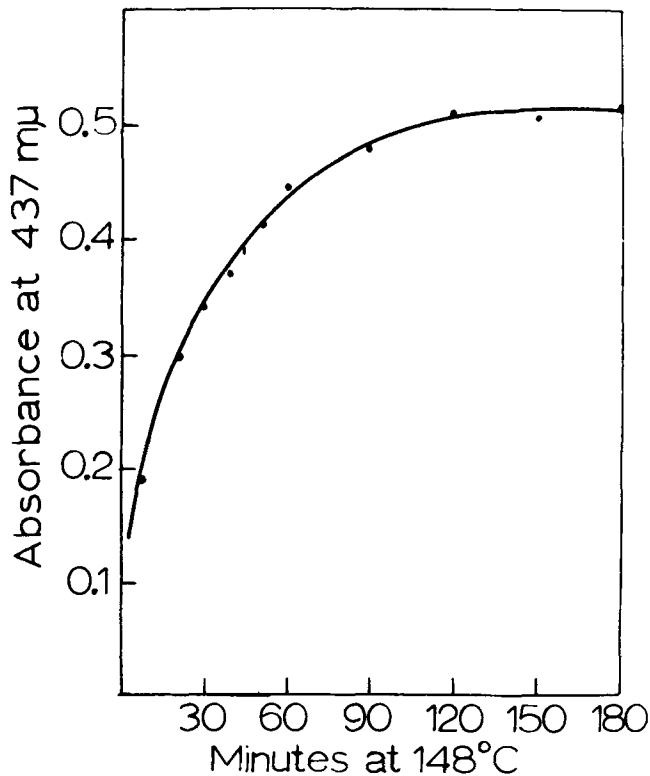


FIG. 2. Influence of roasting time at 148 C on thiobarbituric acid reactant.

Quantitative values for total pyrazines in several types of roasted cocoa beans as reported by Reineccius et al. (32) are presented in Table IV. All samples had been roasted 30 min at 150 C. The wide range of values shown, 142 μg to 698 $\mu\text{g}/100$ g beans, reflects the influence of the fermentation process on the formation of pyrazine precursors. Beans in Ghana and Brazil (Bahia) are usually fermented quite thoroughly; Ecuadorian Arriba beans characteristically are lightly fermented, while the Mexican Tabasco and Dominican Sanchez beans do not in most instances go through a planned fermentation after harvesting of the pods.

Hydrolysis of sucrose and protein during fermentation to yield reducing sugars and free amino acids is a well

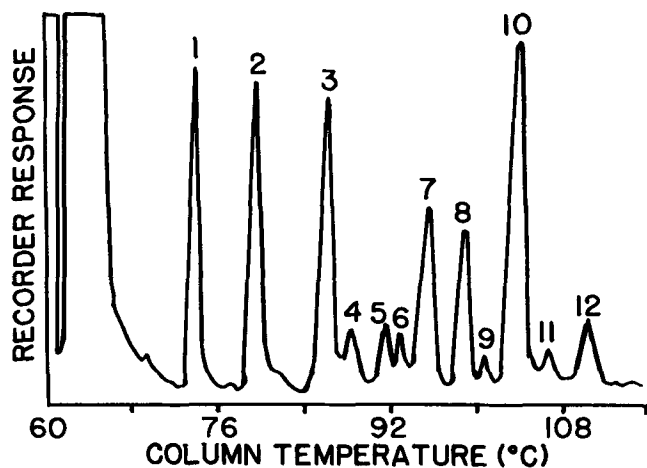


FIG. 3. Gas chromatographic separation of alkylpyrazines in the basic fraction of Ghana cocoa beans (roasted at 150 C for 30 min). Key: (1) pyrazine (internal standard); (2) acetoin and methyl pyrazine; (3) mixture of 2,5-dimethyl, 2,6-dimethyl and ethyl pyrazines; (4) 2,3-dimethyl pyrazine; (5) 2-ethyl-6-methyl pyrazine; (6) 2-ethyl-5-methyl pyrazine; (7) trimethyl pyrazine; (8) 2,5-dimethyl-3-ethyl pyrazine; (9) 2,3-dimethyl-6-ethyl pyrazine; (10) tetramethyl pyrazine; and (11,12) contamination.

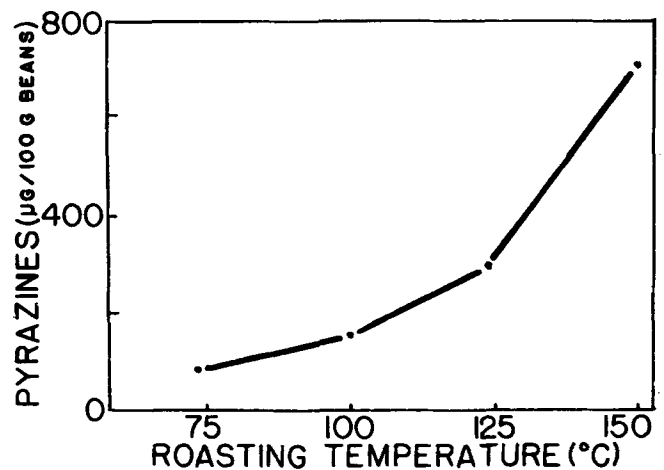


FIG. 4. Influence of roasting temperature on the concentration of alkylpyrazines in Ghana cocoa beans.

documented occurrence (26,28). However our studies suggest that the more rapid and greater alkylpyrazine-generating potential of fermented beans cannot be explained adequately strictly on the basis of reducing sugar and free amino acid concentrations.

Average sucrose and reducing sugar concentrations for several batches of four types of cocoa beans are listed in Table V (39). These data indicate that the concentration of reducing sugars in unroasted beans does not necessarily correlate well with fermentation, at least for pooled shipments of the commodity as received in the consuming country. Since several days under the sun may be needed to dehydrate wet cocoa beans, enzymatic changes within the cotyledon and microbial breakdown of mucilaginous material can be expected to proceed to a certain extent, even though a fermentation step is not carried out. The presence of a significant quantity of reducing sugars in unfermented beans seems inevitable, especially since sucrose, the only sugar in the cotyledons of freshly opened pods, inverts readily when exposed to the elements.

Comparisons among free amino acid fractions of various types of beans are not given in detail in this paper. However trends similar to those described for the sugars were found, in that beans from countries where the crop is not fermented did undergo proteolysis during drying, as evidenced by the significant levels of free amino acids found.

From the foregoing it is obvious that we must look beyond the sucrose and protein hydrolysis stages to gain an insight concerning the development of precursors for the

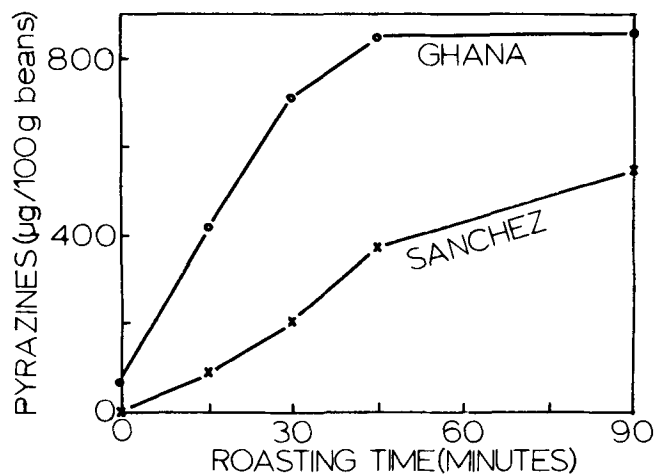


FIG. 5. Comparison of alkylpyrazine formation during roasting (150 C) of fermented (Ghana) and unfermented (Sanchez) cocoa beans.

TABLE IV

Concentration of Alkylpyrazines in
Several Varieties of Roasted Cocoa Beans

Variety	Beans, $\mu\text{g}/100 \text{ g}$
Ghana	698
Bahia	587
Samoa	358
Arriba	238
Sanchez	233
Tabasco	142

alkylpyrazines. Referring again to Table V, although sucrose was almost completely consumed during fermentation of Ghana and Bahia beans, a corresponding increase in reducing sugars was not apparent, at least when compared to unfermented Sanchez beans. This implies that, when beans are subjected to a controlled fermentation, reducing sugars from the inversion of sucrose are metabolized further, to yield more active intermediates for the nonenzymatic browning reactions initiated during roasting. This also applies to the amino acid fractions, since ammonia nitrogen was found to be consistently greater in fermented beans.

In his study of alkylpyrazine formation during roasting (Fig. 5) Reineccius et al. (32) detected no major differences between unfermented and fermented beans with respect to the rate of depletion of either reducing sugars or free amino acids. Reducing sugars were consumed completely before the free amino acids and this agrees with the findings of Rohan and Stewart (40). Sucrose concentration decreased only slightly, which is in conflict with their claim of significant sucrose destruction during roasting. It is of interest to note the report of Feldman et al. (41) on the almost complete disappearance of sucrose when coffee is roasted, whereas the data of Newell et al. (38) for peanuts agrees more with our cocoa results.

Cocoa Sugars

It is this author's opinion that the GLC sugars analyses of Reineccius et al. (39) reported in Table VI contain data of profound importance with respect to the precursors of the alkylpyrazines and chocolate flavor volatiles in general. The fact that the ketoses, fructose and sorbose, dominated the sugars fraction of fermented Bahia and Ghana beans suggests a preferential metabolism of glucose during fermentation or its enzymatic conversion to a ketose. These beans contained 17 and 7 times more ketose sugar than glucose, respectively. In unfermented Sanchez beans the more one to one split expected from sucrose hydrolysis was observed, while the ratio for lightly fermented Arriba beans was in between.

Model systems studies have shown that fructose yields more volatile material than glucose (42) and, more specifically, alkylpyrazines (43) when subjected to thermally initiated nonenzymatic browning. The much higher ketose content in Ghana beans compared to Sanchez beans could account for the more rapid and greater yield of alkylpyrazines during roasting of the former, as illustrated in Figure 5.

Based on the large number of compounds identified in the aroma fraction (Tables I and II), chocolate must certainly be credited as one of the most complicated natural flavors. While chocolate manufacturers can usually agree on which flavor notes constitute defects to be avoided, there is little unanimity of opinion regarding optimum flavor characteristics. Through bean selection and blending, and process modifications in the chocolate factory, nuances in flavor are imparted purposely which are ultimately judged by the consumer as to their degree of desirability.

Nonvolatile Acids

Reference has been made with varying emphasis to

TABLE V

Sugars Content of Unroasted Cocoa Beans

Sugars	Beans, mg/100 g			
	Sanchez	Arriba	Bahia	Ghana
Total sugars	1856	1332	1308	858
Sucrose	1000	683	55	120
Reducing sugars	747	510	855	612

TABLE VI

Percentage Composition of the Sugars
Fraction of Unroasted Cocoa Beans

Sugar	Per cent by wt			
	Sanchez	Arriba	Bahia	Ghana
Glucose	19	14	3	8
Fructose	19	22	52	57
Sorbose	2	3	10	6
Sucrose	54	51	4	14
Pentitol	2	5	3	3
Mannitol	2	2	21	9
Inositol	2	2	4	14

occurrences in both the producing country and the chocolate factory that affect chemical changes related to flavor. A variable not mentioned previously but deserving attention concerns the nonvolatile acids of cocoa beans (22).

Citric acid concentration may be three times that in milk sherbet to which it is added to impart tartness, and some well fermented samples of beans will have more lactic acid than develops during the setting of cottage cheese curd. Lots of phosphoric acid is also found in beans when the acids are precipitated as lead salts and analyzed by GLC after conversion to trimethylsilyl ethers. Yet chocolate is not nearly as tart as we might predict on the basis of organic acid content. This can be rationalized quite easily, but it is not within the scope of this symposium. What needs to be emphasized, however, is that during the early stages of roasting, before moisture gets down to the final 1-2% level, the water phase undoubtedly has a low pH which varies depending on organic acid content. The removal of moisture during roasting can be visualized as a steaming process, and the transfer of moisture and its soluble constituents from the interior of the bean to the surface and all that this entails must be an important part of the synthesis of chocolate flavor.

Cocoa Lipids

It would be inappropriate to conclude this discussion without mention of the role of cocoa lipids in the various interactions of chocolate flavor. Attempts by ourselves and others to relate the lipids of cocoa to the formation of aroma volatiles suggest that they play a minor role, except when flavor defects are involved (8). However this doesn't mean that cocoa fat is not important to flavor in chocolate confections. Cocoa fat is the continuous phase and coats the sugar crystals and nonfat cocoa constituents to impart lubricating, unctuous properties. Distribution of aroma compounds between lipid and polar phases is undoubtedly an important factor affecting release of volatiles and the perception of chocolate flavor. Since processing after roasting is essentially grinding and mixing, surface phenomena involving the lipid coating must determine what is retained and lost with respect to aroma constituents.

Cocoa fat might also be considered a package or protective coating for chocolate flavor. Flavor stability is truly remarkable when we consider the fact that chocolate and chocolate coatings are 35-50% by weight lipid. An understanding of why this is so could have implications well beyond the realm of confectionery products.

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