Casing materials—cocoa (Part I)

By G.C. Harllee and J.C. Leffingwell

The importance of cocoa powder as a casing material for tobacco is well known (1).* Virtually all blended cigarettes of the American type employ casing materials such as sugar and/or fruit extracts, licorice, and cocoa. These materials are used to mellow nicotine harshness and enhance the flavor of the tobaccos (2). From a historic standpoint, the use of these materials have their origin traced back to use on chewing tobacco and smoking tobaccos which preceded the blended cigarette.

Cocoa beans are grown commercially in more than 45 countries, but supply is basically controlled by the five major producing countries which account for more than 75% of world production (3): Brazil, 18%; Ghana, 24%; Ivory Coast, 17%; Nigeria, 13%; Cameroun, 7%. while cocoa bean producing countries consume only about 7% of the world supply,

Western Europe accounts for nearly 39% of total consumption, followed by North America, 29%; Eastern Europe and the Soviet Union, 15.5%; and the Asian countries, 5%.

Since World War II, cocoa production has steadily increased in a manner resulting in a relatively stable supply/demand situation for cocoa products at attractive prices. Today, world consumption of cocoa beans exceeds by 250% that of the years
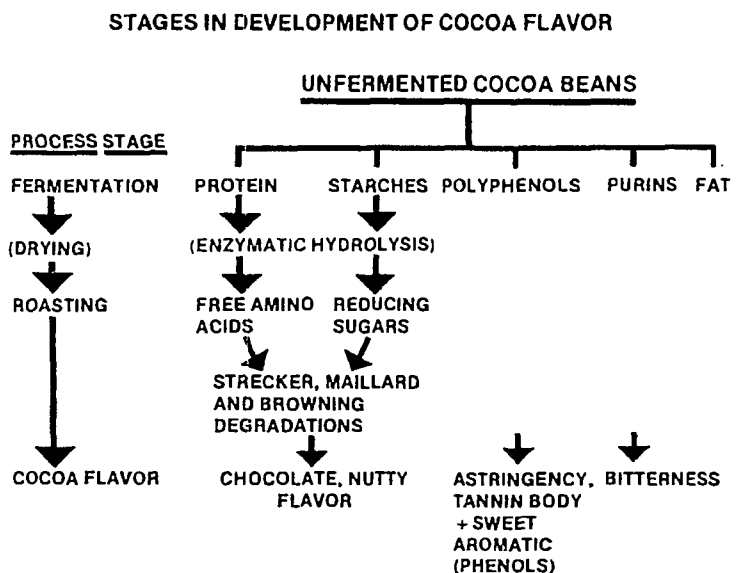
immediately following the war.

In the mid-1970s, several events, which had been in the making for a number of years, caused major cocoa users to reassess the long-range supply/demand picture. Basically, these factors may be listed as follows (not in order of importance):

1. Political emergence of developing nations.
2. Inflation rates (real).
3. Increased purchasing power of

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Bibliographical references will be at the end of the second part of this two-part article.

Chart 1.

STAGES IN DEVELOPMENT OF COCOA FLAVOR

Eastern Europe.

4. Energy crisis and resulting devaluation of U.S. dollar in international monetary exchange rates.

5. Agricultural development programs in cocoa producing countries.

In 1964, North America and Europe accounted for 72% of world cocoa consumption; by 1972, this had decreased to 68% while consumption by Communist Bloc countries had risen from 10.7% to 15.5% of the world total. Perhaps more important, however, have been the effects of the U.S. trade imbalance, owing to energy imports. This has meant that cocoa is now attractively priced to countries with more favorable exchange rates than those of the U.S., which has suffered immensely in its ability to purchase international commodities at reasonable prices.

This is strikingly shown in comparing the exchange rates of U.S. dollars to Swiss Francs in the years 1969-1978, when the relative value of the dollar slumped to 1/3 of its former value. The immediate effect, of course, has been much higher prices for U.S. purchasers.

Thus, today, cocoa pricing is a factor more of international economics than of weather effects on crop yield in producing countries.

Even with the international economic restructuring that is occurring as a factor, world consumption of cocoa products is still increasing. Demand projections require that the five major producing countries increase supplies by nearly 30% in the next 10 years. Any shortfall in the aggressive agricultural programs in these developing nations could result in a situation of shortages, commodity speculation, and higher prices of a magnitude greater than that experienced in the last five years.

Overall economic and supply considerations have caused grave concern among cocoa users and have prompted major research efforts on cocoa composition with the view toward development of economically attractive extenders and replacements.

This paper is written to provide an overview of certain aspects of the chemical composition of cocoa

Chart 2.

Protein(s) ∿∿∿∿∿▸Amino Acids

Polysaccharides ∿∿▸ Reducing Sugars

Table 1.

AMINO ACID COMPOSITION OF DEFATTED COCOA BEANS
(BAHIA BEANS; in $g/100g$ beans)

Amino Acid	(Total hydrolysate) Unfermented	Fermented	(FREE Amino Acid) Unfermented	Fermented
Lysine	2.34	2.36	0.027	0.204
Histidine	0.49	0.47	0.034	0.026
Arginine	1.62	1.48	0.024	0.134
Aspartic Acid	2.60	2.71	0.189	0.325
Threonine	0.66	0.63	0.009	0.074
Serine	0.60	0.62	0.035	0.101
Glutamic Acid	3.60	3.59	0.122	0.190
Proline	1.13	1.14	0.045	0.092
Glycine	1.00	1.00	0.032	0.074
Alanine	0.90	0.88	0.042	0.154
Valine	1.28	1.32	0.008	0.083
Methionine	0.21	0.21	0.012	0.026
Isoleucine	0.71	0.74	0.018	0.067
Tyrosine	0.61	0.65	0.025	0.116
Phenylalanine	1.18	1.17	0.024	0.228
Leucine	1.50	1.48	0.018	0.307
TOTAL	20.53	20.45	0.664	2.201

N. Maravalhas, Int. Choc. Review, 27, 22 (1972)

Chart 3.

RELATIONSHIP BETWEEN PYRAZINE FORMATION AND REDUCTION OF AMINO ACIDS AND REDUCING SUGARS IN ROASTING OF GHANA COCOA BEANS

Roasting Time (Min. at 150°c)
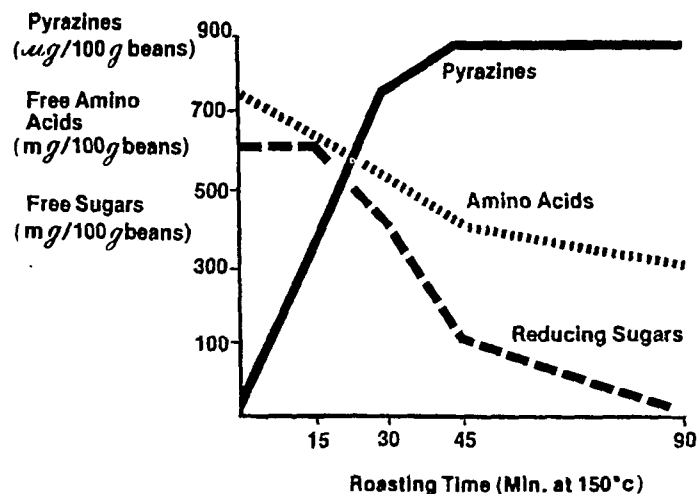
G. A. Reineccius, P. G. Keeney and W. Weisberger, J. Agr. Food Chem., 20, No. 2, 202-206 (1972)

which will be of interest to the tobacco industry.

In order to understand the development of cocoa (or chocolate) flavor, it is necessary to briefly review the steps which occur in processing ripe cocoa beans after they are harvested (4).

Following harvest from the cocoa tree (*Theobroma cacao L.*), the cocoa pods are split open. The pulp-covered beans are bulked and the mass allowed to ferment (in a manner not dissimilar to the classic methods of cigar tobacco fermentation). After a period ranging from 1-5 days fermentation, the beans are freed from the fermented pulp and spread out to dry in the tropical sun. Following a slow process of air drying and cleaning, the cocoa beans are prepared for shipment from the agricultural centers. The process of fermentation causes marked changes in chemical composition within the cocoa bean cotyledon (shell). In the initial fermentation, enzymatic processes convert polysaccharides to reducing sugars and proteins to free amino acids (4, 5). During the fermentation stages, nearly 10% of the total polysaccharides and protein content is converted to reducing sugars and free amino acids.

The effect of fermentation on the protein portion of cocoa beans is illustrated in **Table 1** by looking at the amino acid composition of Bahia cocoa beans before and after fermentation, which shows a nearly fourfold increase in free amino acids (6). Rohan and co-workers have shown that depending on duration of the fermentation period, as much as

CHANGE IN FREE AMINO ACID LEVELS IN FERMENTED GHANA COCOA BEANS DURING ROASTING FOR 30 MINUTES AT 150°C

Amino Acid	Unroasted (mg/100g)	Roasted (mg/100g)	Δ (%)
Lysine	58.3	36.4	-48
Histidine	7.6	6.4	-16
Arginine	41.3	29.5	-29
Aspartic Acid	55.2	39.6	-28
Threonine	21.7	14.8	-32
Serine	55.6	35.2	-37
Glutamic Acid	64.0	31.4	-51
Proline	32.2	24.9	-23
Glycine	7.9	7.5	-5
Alanine	57.0	42.6	-25
Valine	46.2	35.9	-22
Isoleucine	30.1	25.8	-14
Leucine	103.5	73.6	-29
Tyrosine	43.4	35.9	-17
Phenylalanine	95.7	73.6	-23
	719.7	513.1	-29

Adapted from G.A. Reineccius, P.G. Keeney, and W. Weissberger, J. Agric. Food Chem., 20(2), 202-206 (1972)

Table 2.

100% conversion of sucrose to the reducing sugars, glucose and fructose, may occur (7).

The formation of a desirable cocoa flavor on processing is affected by numerous factors, among which are genetic variety, bean maturity prior to harvest, and many other factors analogous to those encountered in tobacco agricultural practices which affect chemical composition. These factors as well as processing techniques affect the availability of the requisite flavor precursors (6-21).

At a point prior to the roasting in cocoa bean processing, the characteristic cocoa (chocolate) aroma has not yet developed. This is formed during the subsequent heat treatment of the cocoa beans. During roasting a dramatic reduction of both free amino acids and reducing sugars occurs, with a concomitant increase in the highly flavorful pyrazines. This is illustrated for the roasting of Ghana beans at 150° in **Chart 3** (22).

Table 2, adopted from the data of Reineccius (22), shows in detail the changes in free amino acids level

which occur during roasting. It should be noted that roasting for 30 minutes decreases the overall free amino acid level by nearly 30% but that some amino acids are degraded much more rapidly than others.

The heat induced browning reaction of amino compounds and sugars produces a multiplicity of volatile and non-volatile products (Chart 4), many of which contribute to the characteristic cocoa/chocolate aroma (5).

It is now generally accepted that the heat induced Maillard and Strecker reactions of amino acids and reducing sugar flavor precursors are largely responsible for formation of cocoa aroma. Among some of the well characterized compounds which contribute to the roast aroma are the pyrazines (23). Chart 5 illustrates the formation of specific pyrazines on roasting Ghana cocoa beans (22).

One mechanism for the formation of pyrazines from amino acids and carbonyl comonents derived via browning degradation of sugar is shown in Chart 6 for the formation of a dimethyl pyrazine and a dimethyl ethyl pyrazine.

Following roasting, the cocoa beans are cracked open and the shell removed and sold as a by-product. The internal part or "cocoa nib" is then ground and pressed. The pressing removes a large part of the cocoa butter which goes almost entirely into chocolate (candy) manufacture. (Prior to pressing, cocoa butter fat constitutes better than 50% of the cocoa nib weight.) The remaining part of the cocoa nib is then pulverized, sized and sold as cocoa powder (24). A typical range of cocoa powder analysis is shown in Table 3 (25).

As may be noted, cocoa powder is made up primarily of crude protein and amino acids, the astringent tannin-like polyhydroxyphenols, starch, sugars, cocoa butter fat, miscellaneous cell wall constituents, and the bitter principles, theobromine and caffeine.

Cocoa butter is composed almost entirely of fatty acid triglycerides, which possess novel physical properties prized in chocolate candy man-

ufacture. Tables 4 and 5 show the composition of cocoa butter (25).

In tobacco smoking products, the organoleptic properties of cocoa butter are that of a smoothing, yet substantially enhanced, tobacco flavor which we propose is owing to entrapment of tobacco flavor volatiles by agglomeration in the cocoa butter aerosol droplets in the smoke

Chart 4.

TWO PATHWAYS OF REDUCING SUGARS
IN THE MAILLARD REACTION

EFFECT OF ROASTING TIME ON PYRAZINE FORMATION IN GHANA COCOA BEANS

(μg/100 g beans)

Roasting Time (Min. at 150°c)

Total Pyrazines
Tetramethylpyrazine
Dimethylpyrazines
Trimethylpyrazine

G.A. Reineccius, P.G. Keeney and W. Weissberger, J. Agr. Food Chem., 20, No. 2, 202-206 (1972).

Chart 5.

Chart 6.

THE STRECKER REACTION ➔ MAILLARD REACTION

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mainstream. A similar effect is observed with the major tobacco hydrocarbon, neophytadiene, which itself possesses no specific flavor properties, but acts as a flavor carrier in the smoke aerosol. This proposal takes on added credence when one considers that no known compound in excess of molecular weight 350 is known to possess individual flavor characteristics.

Schlotzhauer (26) has recently published results on the pyrolysis of cocoa powder in which the cocoa butter fat yielded stearic and palmitic acid at temperatures which might be encountered in a burning cigarette. However, the laboratory method of pyrolysis does not simulate the dynamic system encountered in the burning cigarette and under no circumstances has the flavor effect of either of these acids been detected by expert smokers when evaluating cigarettes spiked with cocoa butter. Although a degree of pyrolysis of cocoa butter fat may occur, we do not feel that it is sufficient to produce a flavor effect in the cigarette mainstream smoke.

Although cocoa butter substitutes have now found an important place in chocolate manufacture (27-28), we are not aware of any widespread use in the tobacco industry, primarily be-

COMPOSITION OF COCOA POWDER

	%
Fat (cocoa butter)	11-23
Protein (1)	18-23
Theobromine	2.0-2.5
Caffeine	0.3-0.4
Polyhydroxyphenois	10.0-12.5
Starch	10.0-12.5
Sugars	1.5-2.0
Cell Wall Constitutents	18.0-22.5
Organic Acids	3.4-4.2
Ash	5.0-10.0
Moisture	4.0
Calories (2)	200-300

1. Crude protein content, corrected for nitrogen from the purines
2. per 100 g.

Table 3.

APPROXIMATE COMPOSITION OF COCOA BUTTER

TriGlyceride	%
2-Oleopalmitostearin	57-60
2-Oleodistearin	20-23
Dioleostearin	5-6
Dioleopalmitin	6-8
Others	4-6

Table 4.

APPROXIMATE FATTY ACID COMPOSITION (g/100g COCOA BUTTER)

Oleic Acid (C-18')	33.1
Stearic Acid (C-18)	33.0
Palmitic Acid (C-16)	24.8
Linoleic Acid (C-18")	3.2
Arachidic Acid (C-20)	0.8
Palmitoleic Acid (C-16')	0.3
Myristic Acid (C-14)	0.2

Table 5.

cause the flavor effect in smoke is different than for cocoa butter. In the case of most substitutes for cocoa butter, pyrolysis products are detected in the smoke flavor (29).

The second and concluding part of this article will appear in the March 23 issue.