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# Casing Materials—cocoa (Part II)

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The volatile components in cocoa have been the subject of numerous investigations reported since 1964, the most comprehensive of which are the works of Vitzthum, et. al. (30) Dietrich, et. al (31). Flament, et. al. (30), Marion, et. al. (33), Van Praag, et. al (34), Van der Wal, et. al. (35), and Stoll, et. al. (36). Considerable emphasis in these studies has been on the analysis of the basic (pH) fraction of cocoa volatiles which possess a roasted, nutty, chocolate type aroma.

As a part of our work, we did a comparison of cocoa volatiles with known volatiles in tobacco and tobacco smoke (1). In summary, we found that the volatile constituents of cocoa are, in the majority, identical or analogous to natural tobacco or tobacco smoke constituents. Table 6 provides an overview of the percentage of each class of compound found in cocoa which is also found in tobacco and tobacco smoke, while Table 7 provides the numerical comparison within each class. Thus 59% of all known cocoa volatiles are also found in tobacco or tobacco smoke.

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In retrospect, now that we possess a large portion of knowledge about cocoa constituents, it is not really surprising that the early tobacco flavoring pioneers found this inexpensive flavor commodity (cocoa) to be so complimentary to the smoking properties of *Nicotiana tabacum*.

The smoking flavor properties of many of the reported volatile cocoa constituents have previously been reported by Leffingwell (37-38) and it is not the purpose of this paper to review these organoleptic evaluations in detail. However, several brief general comments on some of the classes of reported compounds is in order, in order to comprehend the potential contribution to the overall cocoa flavor when used in tobacco products for smoking.

Within the reported acids, we find that the lower fatty acids ($C_2$ - $C_{10}$) and the phenylacetic acids contribute in a positive manner to the improvement of tobacco flavor. Among the reported alcohols, 1-octen-3-ol, geraniol, linalool, and the phenylethanols are positive flavorants. The aldehydes (isobutyraldehyde, the methylbutanals, and phenylacetaldehyde) are important tobacco flavorants. The class of esters include such materials as ethyl and methyl phenylacetates which contribute positive honey, flue-cured type notes to tobacco. Ketones, such as diacetyl and 2,3-pentanedione, provide buttery-like notes to tobacco, while 2-acetylfuran provides a

Table 6. MAJOR COCOA VOLATILE CONSTITUENTS

| | % Also Present In | |
|---|---|---|
| | Tobacco Leaf | Tobacco Smoke |
| Alcohols | 74 | 59 |
| Aldehydes | 55 | 59 |
| Acids | 84 | 78 |
| Esters | 35 | 20 |
| Ketones | 59 | 53 |
| Amines | 56 | 100 |
| Pyrazines | 16 | 25 |
| Hydrocarbons | 47 | 85 |
| Pyrroles | 44 | 67 |
| Ethers | 6 | 13 |
| Phenols | 86 | 86 |
| Pyridines | 43 | 71 |
| Lactones | 83 | 33 |
| Sulfur Compounds | 7 | 36 |

VOLATILE CONSTITUENTS OF COCOA
ALSO PRESENT IN TOBACCO OR TOBACCO SMOKE

| | Tobacco | Tobacco Smoke | Tobacco/ Tobacco Smoke | Tobacco/ Tobacco Smoke (%) |
|---|---|---|---|---|
| Hydrocarbons (34) | (16) | (29) | (31) | (91) |
| Alcohols (27) | (20) | (16) | (24) | (69) |
| Aldehydes (22) | (12) | (13) | (16) | (73) |
| Pyridines (7) | (3) | (5) | (6) | (86) |
| Pyrazines (64) | (10) | (16) | (16) | (25) |
| Ketones (34) | (20) | (18) | (26) | (76) |
| Volatile Acids (37) | (31) | (29) | (32) | (86) |
| Esters (55) | (19) | (11) | (22) | (40) |
| Lactones (6) | (5) | (2) | (5) | (83) |
| Amines (9) | (5) | (9) | (9) | (100) |
| Pyrroles (9) | (4) | (6) | (6) | (67) |
| Ethers (16) | (1) | (2) | (2) | (13) |
| Miscellaneous (11) | (1) | (3) | (3) | (27) |
| Phenols (7) | (6) | (6) | (6) | (86) |
| Sulfur Compounds (14) | (1) | (5) | (5) | (36) |
| Total (252) | (154) | (170) | (209) | (59%) |

Table 7.

burley-like note and 3-methyl-cyclopentan-1,2-dione (cyclotene) provides a rich maple characteristic. The lactones reported in cocoa are nearly all very positive in improving tobacco flavor. Phenols, in general, provide a sweetening effect in tobacco when used at extremely low levels, although eugenol provides a clove-like spiciness. One of the most interesting classes of compounds as tobacco flavorants are the pyrazines, which contribute nutty, earthy, roasted, and chocolate notes. The pyridines also contribute to both cocoa and tobacco flavor. For example, 2-methylpyridine provides a burley note to tobacco while pyridine contributes a flue-cured note. The pyrroles are relatively weak flavorants, but may contribute to sweet ketonic notes found in tobacco. Sulfur compounds are very potent flavor materials and they are found in cocoa in quantities suggesting that they contribute to the roast aroma. Very few sulfur compounds have been reported in tobacco or smoke and their contribution as tobacco flavorants has not been studied in any detail.

These limited comments regarding flavor lead us now to examine in detail the volatile compounds found in cocoa and their occurrence in tobacco or tobacco smoke. Those materials for which a tobacco flavor evaluation has been reported are also indicated in the following tabulation (Tables 8-27).

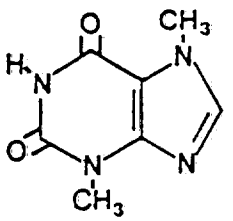
One of the most interesting classes of compounds found in cocoa are the nitrogenous bitter principles which consist of theobromine, caffeine and a series of diketopiperazines (Chart 7).

The latter compounds are produced by the heat induced cyclodimerization of free amino acids. Eleven diketopiperazines were identified by Pickenhagen, et. al. (39) in cocoa while Schumacher, et. al. (40) has proposed two in tobacco smoke (Table 25). Interestingly, one of the major diketopiperazines reorted in cocoa is also proposed as a smoke constituent.

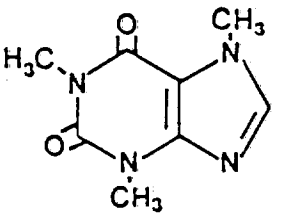
While the diketopiperazines are bitter principles themselves, this bitterness is dramatically enhanced synergistically by theobromine and the combination is of key importance to the bitter character of cocoa (39).

Chart 7.

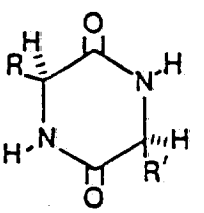
BITTER PRINCIPLES IN COCOA



THEOBROMINE (1.5%)



CAFFEINE (0.15%)



DIKETOPIPERAZINES (10 isolated, ca. 0.05% by weight)
(synergistic to Theobromine bitterness)

Tables 29-31 show the additive smoking flavor evaluations of a series of compounds reported as cocoa volatiles but for which no smoking flavor evaluation had previously been reported in the literature. These evaluations were carried out by procedures previously reported (37, 38).

Table 32 shows the relative concentration of the major non-volatile organic acids in cocoa beans, as reported by Weissberger, et. al. (41). The relative concentration of non-volatile acids appears to be generally in the order citric ▶ phosphoric ▶ oxalic ▶ lactic ▶ malic ≅ succinic = tartaric ≅ gluconic. Although roasting of cocoa beans does not appreciably change the relative acid concentrations, the fermentation step causes a decrease in citric acid and an increase in lactic acid.

The role of these acids contributed by cocoa in tobacco flavor casing is considered to be essentially nil.

The relative amount of protein and free amino acids present in cocoa may vary somewhat, depending on the source of the various commercial varieties of cocoa beans as well as with bean maturity and degree of fermentation. The variation in free amino acids in unroasted beans has been linked to observed differences in flavor quality after roasting (for beans from various sources) (21). Nevertheless, the amino acid composition of the protein fraction of

Tables on page 21
Text on page 26

COCOA VOLATILES

| Acids | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| Formic Acid | x | x | x | x |
| Acetic Acid | x | x | x | x |
| Propionic Acid | x | x | x | x |
| Lactic Acid | x | x | x | x |
| 2-Methylpropionic Acid | x | x | x | x |
| Butanoic Acid | x | x | x | x |
| Crotonic Acid | x | x | x | x |
| 2-Methylbutanoic Acid | x | x | x | x |
| 3-Methylbutanoic Acid | x | x | x | x |
| 2-Hydroxy-3-methylbutanoic Acid | x | x | | x |
| Pentanoic Acid | x | x | x | x |
| 4-Methylpentanoic Acid | x | x | x | |
| 2-Hydroxy-4-methylpentanoic Acid | x | x | | x |
| Hexanoic Acid | x | x | x | x |
| Heptanoic Acid | x | x | x | x |
| Octanoic Acid | x | x | x | x |
| Nonanoic Acid | x | x | x | x |
| Decanoic Acid | x | x | x | x |
| Lauric Acid | x | x | x | x |
| Myristic Acid | x | x | x | x |
| Palmitic Acid | x | x | x | x |
| 2-Hydroxy-3-methylglutaric Acid | x | | | |
| Benzoic Acid | x | x | x | x |
| 2-Methoxybenzoic Acid | x | x | | e |
| 4-Hydroxybenzoic Acid | x | x | x | e |
| 4-Methoxybenzoic Acid | x | | | |
| 4-Hydroxy-3-methoxybenzoic Acid | x | x | x | |
| 3,5-Dimethoxy-4-hydroxybenzoic Acid | x | x | x | |
| 3,4-Dihydroxybenzoic Acid | x | x | x | |
| Phenylacetic Acid | x | x | x | x |
| 2-Hydroxyphenylacetic Acid | x | x | x | |
| 4-Hydroxyphenylacetic Acid | x | x | x | |
| 4-Hydroxyphenylpropionic Acid | x | | x | |
| 4-Hydroxycinnamic Acid | x | x | x | |
| 4-Hydroxy-3-methoxycinnamic Acid | x | x | x | x |
| 2-Methoxyphenylacetic Acid | x | | | |
| 4-Methoxyphenylacetic Acid | x | | | |

Table 8.

COCOA VOLATILES

| Alcohols | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| Methanol | x | x | x | |
| Ethanol | x | x | x | x |
| 1-Propanol | x | | x | x |
| 2-Propanol | x | | x | x |
| Isobutanol | x | | x | x |
| 1-Butanol | x | x | x | x |
| 2-Butanol | x | | x | x |
| 3-Methylbutanol | x | x | | |
| 1-Pentanol | x | x | | x |
| 1-Hexanol | x | x | | x |
| 2-Heptanol | x | (isomer) | | x |
| 1-Octanol | x | x | | x |
| 1-Octen-3-ol | x | x | | x |
| Geraniol | x | x | x | x |
| Linalool | x | x | x | x |
| Benzyl alcohol | x | x | x | x |
| 1-Phenylethanol | x | x | x | x |
| 2-Phenylethanol | x | x | x | x |
| 2-Phenylpropan-2-ol | x | | | x |
| 2-Methyl-3-phenylpropan-2-ol | x | | | x |
| Menthol | x | x | x | x |
| α-Terpineol | x | x | | x |
| 4-Terpineol | x | | | x |
| Borneol | x | x | x | x |
| Furfuryl alcohol | x | x | x | x |
| 2,3-Butanediol | x | x | x | • |
| Linalool oxide | x | x | | x |

Table 9.

COCOA VOLATILES

| Amines | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| Methylamine | x | x | x | |
| Dimethylamine | x | | x | |
| Trimethylamine | x | x | x | |
| Ethylamine | x | x | x | |
| Isobutylamine | x | x | x | |
| Triethylamine | x | | x | |
| sec-Butylamine | x | | x | |
| Isoamylamine | x | | Isomer | x |
| Phenylethylamine | x | x | x | x |

Table 11.

Table 10.

COCOA VOLATILES

| Aldehydes | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| Acetaldehyde | x | x | x | x |
| Acrolein | x | | x | |
| Propanal | x | x | x | x |
| Isobutyraldehyde | x | x | x | x |
| 2-Methylprop-2-enal | x | | x | |
| 1-Butanal | x | x | x | x |
| Crotonaldehyde | x | x | x | |
| 2-Methylbutanal | x | x | x | x |
| 3-Methylbutanal | x | x | x | x |
| Hexanal | x | x | x | x |
| 5-Methyl-2-isopropylhex-2-enal | x | | | x |
| Octanal | x | | | x |
| 2,4-Octadienal | x | | | |
| Nonanal | x | | | x |
| Decanal | x | x | | x |
| Citronellal | x | | x | x |
| Benzaldehyde | x | | x | x |
| Phenylacetaldehyde | x | x | | x |
| 2-Phenylbutenal | x | x | | x |
| 4-Methyl-2-phenylpent-2-enal | x | | | |
| 5-Methyl-2-phenylhex-2-enal | x | | | |
| Pentanal | x | x | x | x |

Table 12.

COCOA VOLATILES

| Esters | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| Ethyl-3-heptenoate | x | | | |
| Ethyl octanoate | x | x | | x |
| Ethyl decanoate | x | x | | x |
| Ethyl dodecanoate | x | x | | e |
| Ethyl myristate | x | x | | x |
| Isobutyl benzoate | x | | Isomer | x |
| Ethyl benzoate | x | x | x | x |
| Isoamyl benzoate | x | | | x |
| Methyl phenylacetate | x | x | | x |
| Ethyl phenylacetate | x | x | | x |
| Ethyl cinnamate | x | | | x |
| α-Terpinylacetate | x | x | | x |
| Ethyl lactate | x | x | x | x |
| Ethyl-2, 2-diethoxypropionate | x | | | |
| Ethyl-3-ethoxypropionate | x | | | |
| Ethyl-3-methylbutanoate | x | x | x | x |
| Ethyl-2-hydroxybutanoate | x | | | |
| Ethyl-4-methylpentanoate | x | Isomer | | |
| Ethyl-2-hydroxy-4-methylpentanoate | x | | | |
| Ethyl heptanoate | x | | | x |
| Ethyl nonanoate | x | x | | x |
| Methyl-4-methoxybenzoate | x | | | |
| Ethyl succinate | x | | | |
| Diethyl succinate | x | | | x |
| Methyl furan-2 carboxylate | x | | | |
| Ethyl furan-2 carboxylate | x | | | |

## COCOA VOLATILES

| Esters | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| Methyl acetate | x | | x | x |
| Ethyl acetate | x | x | x | x |
| Propyl acetate | x | x | | x |
| Isopropyl acetate | x | | | x |
| Butyl acetate | x | x | x | x |
| Isobutyl acetate | x | | | x |
| 2-Methylbutyl acetate | x | | | |
| Amyl acetate | x | | | • |
| Isoamyl acetate | x | | | x |
| 2-Pentyl acetate | x | | | |
| Neryl acetate | x | | | x |
| Geranyl acetate | x | | | x |
| Linalyl acetate | x | x | | x |
| Benzyl acetate | x | x | x | x |
| Pheny acetate | x | | | • |
| 3-Phenylpropyl acetate | x | | | x |
| Furfuryl acetate | x | | x | x |
| Ethyl propionate | x | x | x | x |
| Amyl propionate | x | | | • |
| Hexyl propionate | x | | | x |
| Ethyl-2-oxopropionate | x | | | |
| Amyl butanoate | x | | | x |
| Hexyl butanoate | x | | | x |
| Ethyl crotonate | x | | | • |
| Ethyl-3-methylbut-2-enoate | x | | | |
| Ethyl-4-oxopentanoate | x | | | |
| Ethyl-4-methylpent-2-enoate | x | | | |
| Ethyl-4-methylpent-3-enoate | x | | | |
| Ethyl hexanoate | x | x | x | x |

Table 13.

## COCOA VOLATILES

| Hydrocarbons | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| Undecane | x | x | x | |
| Dodecane | x | x | x | |
| Tridecane | x | x | x | |
| Tetradecane | x | x | x | |
| Octadecane | x | x | x | |
| β Mycrene | x | | x | x |
| Limonene | x | x | x | x |
| βElemene | x | x | | |
| βPinene | x | | | x |
| Valencene | x | | | |
| Caryophyllene | x | x | | x |
| Benzene | x | | x | |
| Toluene | x | x | x | |
| 1,2-Dimethylbenzene | x | x | x | |
| 1,3-Dimethylbenzene | x | x | x | |
| 1,4-Dimethylbenzene | x | x | x | |
| 1,2,4-Trimethylbenzene | x | x | x | |
| 1,3,5-Trimethylbenzene | x | x | x | |
| 1,2,3,5-Tetramethylbenzene | x | x | x | |
| Styrene | x | | x | • |
| 1-Ethyl-2-methylbenzene | x | | x | |
| 1-Ethyl-3-methylbenzene | x | | x | |
| 1-Ethyl-4-methylbenzene | x | | x | |
| 2-Ethyl-1,4-dimethylbenzene | x | | x | |
| 2,4-Dimethyl-1-vinylbenzene | x | | x | |

Table 15.

## COCOA VOLATILES

| Ethers | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| 1,4-Cineole | x | | | |
| 1,8-Cineole | x | x | | • |
| 2-Methyltetrahydrofuran | x | | x | |
| Furan | x | | | |
| 2-Methylfuran | x | | x | x |
| 3-Phenylfuran | x | | | |
| 1,1-Diethoxyethane | x | | | |
| 1,1-Diethoxy-2-methylpropane | x | | | |
| 1,1-Diethoxy-2-methylbutane | x | | | |
| 1,1-Diethoxy-3-methylbutane | x | | | |
| 1-Ethoxy-1-isobutoxy-3-methyl butane | x | | | |
| 1,1-Diethoxy-3-oxobutane | x | | | |
| 1,1-Dimethoxyphenylethane (acetal) | x | | | |
| Diisoamyl ether | x | | | |
| Benzylethyl ether | x | Me analog | | x |
| Safrole(1-Allyl-3,4-methylene-dioxybenzene | x | | | |

Table 14.

Continued on page 25

COCOA Tables—From page 22

## COCOA VOLATILES

| Ketones | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| 2-Acetyl-5-methylfuran | x | x | x | x |
| 2-Propionylfuran | x | | | |
| 2-Methyltetrahydrofuran-3-one | x | x | | • |
| Tetrahydrofuran-2-one | x | | | |
| 2-Pentanone | x | x | x | x |
| 3-Hexanone | x | | x | x |
| 1-Acetyl-4-isopropenylcyclo-pent-1-ene | x | (dihydro analog) | | |
| 4-Phenylbutan-2-one | x | | x | |
| Maltol | x | x | x | x |

Table 16.

COCOA VOLATILES

| Ketones | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| Acetone | x | x | x | |
| Acetol acetate | x | | x | |
| 2-Butanone | x | x | x | x |
| 3-Hydroxy-2-butanone | x | | x | x |
| Diacetyl | x | x | x | x |
| Trans-3-penten-2-one | x | x | | |
| 2,3-Pentandione | x | | x | x |
| 5-Methylhexan-2-one | x | | | |
| 2-Heptanone | x | x | | x |
| 6-Methyl-5-hepten-2-one | x | x | | x |
| 2-Octanone | x | | x | x |
| 5-Hydroxyoctan-4-one | x | | | x |
| 4,5-Octandione | x | isomer | | |
| 2-Nonanone | x | x | | x |
| 2-Dodecanone | x | | | |
| 3-Heptadecanone | x | | | |
| Acetophenone | x | x | x | x |
| 2-Hydroxyacetophenone | x | x | x | x |
| 4-Methylacetophenone | x | x | x | x |
| 1-Phenylpropan-2-one | x | x | x | |
| 3-Methylcyclopentan-1,2-dione | x | x | x | x |
| 2-Acetyl-4-Isopropenylcyclo-pent-1-ene | x | | | |
| Menthone | x | | | x |
| Camphor | x | x | | x |
| 2-Acetylfuran | x | x | x | x |

Table 17.

Table 18.

## COCOA VOLATILES

| Hydrocarbon | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| Propylbenzene | x | | x | |
| Cumene | x | | x | |
| 1-Isopropyl-4-methylbenzene (Cymene) | x | | x | x |
| 3-Methylbiphenyl | x | | x | |
| Naphthalene | x | | x | |
| 2-Methylnaphthalene | x | x | x | |
| Dimethylnaphthalene(s) | x | | x | |
| Trimethylnapthalene(s) | x | | x | |
| Tetramethylnaphthalene(s) | x | | x | |

## COCOA VOLATILES

| Lactones | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| 4-Hydroxybutanoic acid lactone | x | x | x | x |
| 4-Hydroxy-2-methylbutanoic acid lactone | x | x | | x |
| 4-Hydroxypentanoic acid lactone | x | x | Isomer | x |
| 4-Hydroxyhexanoic acid lactone | x | | | x |
| 4-Hydroxynonanoic acid lactone | x | x | | x |
| 6,7-Dihydroxycoumarin | x | x | x | x |

Table 19.

COCOA Text—from page 19

cocoa reported by Lanteaume in 1972 (25) is considered to be representative and is given in **Table 33.**

As we reported early in this paper, fermentation partially hydrolyses a portion of the protein to free amino acids (**Table 1**) which are the flavor precursors that partially degrade on roasting (**Table 2**) to give cocoa aroma constituents. Even so, cocoa beans may contain between 0.5-1.0% free amino acids after roasting (1-2% in cocoa powder). Inasmuch as we had previously studied a series of amino acids individually as flavor additives for tobacco, we undertook a study on reconstituting the free amino acid fraction of cocoa in the relative proportions found naturally in roasted Ghana cocoa beans for the purpose of smoking evaluation. This is shown in **Table 34.** As noted, the smoking effect at a level perceivable (0.2-0.7%) was that of a drying, enhanced burley character which is not dissimilar to at least one flavor characteristic provided by cocoa in the casing of tobacco. The fact that the level of the added mixture exceeds that which would be naturally occurring in cocoa used in tobacco casing does not negate the possible utility in artificial cocoa substitute. It should be remembered that free amino acids in tobacco products are flavor precursors for components found in tobacco smoke.

Thus, the role of amino acids as flavor precursors in cocoa flavor may be considered analogous to that reported for tobacco by use several years ago (42).

In reviewing the data presented here, it should be noted that we have emphasized the aspects of cocoa which we consider to be important to those involved in the flavoring of tobacco products.

First, the changing aspects of the world economic situation is projected to lead to steadily higher prices for cocoa products. Also, future price increases could be compounded dramatically by a failure to achieve aggressive agronomic programs in the major cocoa producing countries.

We have deliberately ignored specialized aspects of cocoa agricultural and processing techniques (e.g., Dutching) while emphasizing the relationship between cocoa flavor constituents and those of tobacco and tobacco smoke. We have also ignored the subject of the flavonoid or tannin (polyhydroxyphenol) fraction of cocoa, which is known to contribute to the astringent flavor of cocoa and participates in promoting the browning reactions responsible for cocoa flavor.

However, the data presented represent at least some of the important aspects of cocoa composition, as it relates to basic knowledge which may be of interest in relationship to

## COCOA VOLATILES

| Phenols | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| Phenol | x | x | x | x |
| Cresol(s) | x | x | x | x |
| 2,3-Dimethylphenol | x | | | x |
| 4-Ethylphenol | x | x | x | • |
| Guaiacol (2-methoxyphenol) | x | x | x | x |
| 2-Methoxy-4-methylphenol | x | x | x | x |
| Eugenol (4-allyl-2-methoxyphenol) | x | x | x | x |

Table 20.

tobacco flavoring. The gross changes which occur during the fermentation and roasting of cocoa beans have been reviewed and the importance of free amino acids and reducing sugars shown for the formation of numerous cocoa flavor volatiles, such as the important pyrazine class. In addition, the roasting of cocoa beans contributes to the formation of important bitter principles of cocoa, the diketopiperazines. These processes are analogous to those we have previously shown for the formation of natural tobacco flavorants via the browning reactions (42).

A proposal for the observed flavor effect of cocoa butter in smoking products is presented, explaining why this material exhibits a flavor enhancement of the tobacco product on smoking even though the molecular weight of the cocoa butter constituents exceed that normally associated with compounds that exhibit flavor properties.

A comparison of cocoa volatiles with constituents reported in tobacco and tobacco smoke shows that the majority of compounds found in the former are also present in the latter.

The importance of the classes of cocoa volatiles as flavorants is mentioned, but the reader is referred to our more comprehensive works on tobacco smoking evaluations referenced (37, 38) for specific details.

The role of the free amino acid fractions of cocoa in tobacco flavoring has never been reported previously, but in view of the importance found in tobacco itself (42) we find that reconstitution of a typical free amino acid fraction of cocoa exhibits certain aspects shown by cocoa in tobacco casing.

In conclusion, the data presented herein should be of value to those assessing the current state of the art relating to cocoa composition and the specific aspects which contribute to the flavor of cocoa as a casing material for tobacco.

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COCOA VOLATILES

| Pyrazines | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| 2-Methylpyrazine | x | x | x | x |
| 2,3-Dimethylpyrazine | x | x | x | x |
| 2,5-Dimethylpyrazine | x | x | x | x |
| 2,6-Dimethylpyrazine | x | x | x | x |
| 2,3,5-Trimethylpyrazine | x | x | x | x |
| 2,3,5,6-Tetramethylpyrazine | x | x | x | x |
| 2-Ethylpyrazine | x | | x | x |
| 2-Methyl-5-ethylpyrazine | x | x | x | x |
| 2-Methyl-6-ethylpyrazine | x | x | x | x |
| 2-Methyl-6-isoamylpyrazine | x | | | |
| 2-Methyl-6-(2-methylbutyl)-pyrazine | x | | | |
| 2,3-Dimethyl-5-ethylpyrazine | x | | | • |
| 2,3-Dimethyl-5-isoamylpyrazine | x | | | |
| 2,3-Dimethyl-5-(2-methylbutyl)-pyrazine | x | | | |
| 2,5-Dimethyl-3-ethylpyrazine | x | | | |
| 2,5-Dimethyl-3-propylpyrazine | x | | | |
| 2,5-Dimethyl-3,6-diethylpyrazine | x | | | |
| 2,6-Dimethyl-3-ethylpyrazine | x | | | |
| 2,6-Dimethyl-3-isoamylpyrazine | x | | | |
| 2,6-Dimethyl-3,5-diethylpyrazine | x | | | |
| 2,5-Dimethyl-3-isopropylpyrazine | x | | | |
| 2,3,5-Trimethyl-6-ethylpyrazine | x | | | |
| 2,3,5-Trimethyl-6-isoamylpyrazine | x | | | |

Table 21.

COCOA VOLATILES

| Pyrazine | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| 2-Methyl-3-ethylpyrazine | x | | | x |
| 2-Methyl-6-isopropylpyrazine | x | | | |
| 2-Propylpyrazine | x | | | |
| 2-Methyl-3-isopropylpyrazine | x | | | x |
| 2-Methyl-5-vinylpyrazine | x | Isomer | Isomer | x |
| 2-Methyl-5-propylpyrazine | x | | | x |
| 6,7-Dihydro-5H-cyclopentapyrazine | x | | | |
| 2(or 3),5-Dimethyl-6,7-dihydro-5H-cyclopentapyrazine | x | ? | ? | x |
| 2-Methyl-6,7-dihydro-5H-cyclopentapyrazine | x | | | |
| 2,3-Dimethyl-6,7-dihydro-5H-cyclopentapyrazine | x | | ? | x |
| 2-Methyl-3-ethyl-6,7-dihydro-5H-cyclopentapyrazine | x | | | |
| 5,6,7,8-Tetrahydroquinoxaline | x | | | |
| 2-Methyl-5,6,7,8-tetrahydro-quinoxaline | x | | | |
| 5-Methyl-5,6,7,8-tetrahydro-quinoxaline | x | | | |
| 2-Methyl-5-isobutylpyrazine | x | | | x |
| 2-Methyl-6-isobutylpyrazine | x | | | |
| 2,6-Dimethyl-3-isopropylpyrazine | x | | | |
| 2-Ethyl-5-isopropylpyrazine | x | | | |
| 2,5-Diethyl-3-methylpyrazine | x | | | |
| 2,6-Diethyl-3-methylpyrazine | x | | x | |
| 2,3-Diethyl-5-methylpyrazine | | | | |

Table 22.


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Table 23.

## COCOA VOLATILES

| Pyrazine | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| 2-Isopropenylpyrazine | x | | x | x |
| 2-Ethyl-6-propylpyrazine | x | | | |
| 2,5-Dimethyl-3-n-butylpyrazine | x | | | |
| 2,3,5-Triethylpyrazine | x | | | |
| 2,6-Dimethyl-3-n-butylpyrazine | x | | | |
| 2-Methyl-5-acetylpyrazine | x | Isomer | | |
| 2-Ethyl-5-acetylpyrazine | x | | | |
| 2-n-Pentyl-3-methylpyrazine | x | | | |
| 2-n-Pentyl-5-methylpyrazine | x | | | |
| 2-(2'-methylbutyl)-3-methyl-pyrazine | x | | | |
| 2-Isoamyl-3-methylpyrazine | x | | | |
| 2,5-Dimethyl-3-n-pentylpyrazine | x | | | |
| 2,6-Dimethyl-3-n-pentylpyrazine | x | | | |
| 2,6-Dimethyl-3-(2-methylbutyl)-pyrazine | x | | | |
| 2-(2'-Furyl)-pyrazine | x | | x | x |
| 2-Methyl-5-(2'-furyl)-pyrazine | x | | x | x |
| 2-Methyl-6-(2'-furyl)-pyrazine | x | | x | x |
| 2(2'-Furyl-5'-methyl)-5(6)-methyl pyrazine | Tentative | | | |
| 2-(2'Furyl-3'[4],5'-dimethyl)-5(6)-methylpyrazine | Tentative | | | |

Table 24.

| Pyridines | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| Pyridine | x | x | x | x |
| 2-Methylpyridine | x | | x | |
| 3-Vinylpyridine | x | | x | |
| 2-Methyl-5-ethylpyridine | x | | | |
| 2-Acetylpyridine | x | x | x | x |
| 3-Phenylpyridine | x | x | x | |
| 3-Phenylmethylpyridine (2 isomers) | tentative | | | |

Table 25.

## COCOA VOLATILES

| Pyrroles | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| 2-Formylpyrrole | x | x | x | x |
| 2-Formyl-1-methylpyrrole | x | x | x | x |
| 2-Formyl-5-methylpyrrole | x | x | x | x |
| 1-Ethyl-2-Formylpyrrole | x | | x | |
| 2-Formyl-1-pentylpyrrole | x | | isomer | |
| 2-Acetylpyrrole | x | x | x | x |
| 2-Acetyl-1-pentylpyrrole | x | | | |
| 2-Propionylpyrrole | x | x | x | |
| 1-Methoxycarbonylpyrrole | x | | | |

Table 26.

## COCOA VOLATILES

| Sulfur Compounds | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| Methylthiomethane | x | | x | |
| Methyldithiomethane | x | | x | |
| Methyldithioisopropane | x | | x | |
| Methyldithiobenzene | x | | | |
| Methyltrithiomethane | x | | x | x |
| Methyltrithiopropane | x | | | |
| Propyltrithiopropane | x | | | |
| Isobutylthiocyanate | x | | | |
| 3-Methylthiopropanol | x | | | |
| 2-Methylthio-2-methylpropanol | x | | | |
| 5-Methylfurfurylthiomethane | x | | | |
| 4-Methyl(β-hydroxyethyl)thiazole | x | | | |
| 4-Methyl-5-vinylthiazole | x | | (dihydro analog) | x |
| Benzothiazole | x | x | x | x |

Table 27.

## COCOA VOLATILES

| Miscellaneous | Cocoa | Tobacco | Tobacco Smoke | Tobacco Flavor Reference |
|---|---|---|---|---|
| 2-Methyl Quinoxaline | x | | | |
| 2,3-Dimethyl Quinoxaline | x | | | |
| 2,5-Dimethyl Quinoxaline | x | | | |
| Quinoline | x | x | x | |
| 2,5-Dimethyloxazole | x | | | |
| 4,5-Dimethyloxazole | x | | | |
| 2,4,5-Trimethyloxazole | x | | | |
| 2-n-propyl-5-methyloxazole | x | | | |
| Methyl-o-aminobenzoate | x | | | |
| 3-Methylbutane nitrile | x | | x | |
| Benzonitrile | x | | x | |

Table 28.

DIKETOPIPERAZINES FOUND IN COCOA

AND PROPOSED IN TOBACCO SMOKE

| Diketopiperazine | Found in Cocoa (1) | Proposed in Tobacco Smoke (2) |
|---|---|---|
| Cyclo(-Ala-pro) | x(minor) | |
| Cylco(-Pro-leu-) | x(minor) | |
| Cyclo(-Val-phe-) | x(minor) | |
| Cyclo(-Pro-gly-) | x(minor) | |
| Cyclo(-Ala-val-) | x(major) | |
| Cyclo(-Ala-gly) | x(major) | x |
| Cyclo(-Ala-phe-) | x(minor) | |
| Cyclo(-Gly-phe-) | | |
| Cyclo(-Gly-phe-) | x(minor) | |
| Cyclo(-Val-gly) | | x |
| Cyclo(-Asn-phe-) | x(minor) | |
| Cyclo(-Asn-pro-) | x(minor) | |

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## COCOA VOLATILES NOT PREVIOUSLY REPORTED AS TOBACCO FLAVORANTS

| ESTERS | ADDITIVE SMOKE FLAVOR |
|---|---|
| Ethyl crotonoate | Somewhat nutty, drying, brown-sugar aroma |
| Amyl acetate | Weak, banana-fruity, pungent in high concentration |
| Phenyl acetate | Fruity-floral, honey-like, enhances flue-cured smoke aroma |
| Amyl propionate | Weak, fruity |
| Ethyl dodecanoate (T) | Sweet, smoothing, somewhat flue-cured like |
| **PYRAZINES** | |
| 2,3-Dimethyl-5-ethylpyrazine | Cocoa, chocolate note, enhanced burley taste |

Table 29.

Table 30.

## COCOA VOLATILES NOT PREVIOUSLY REPORTED AS TOBACCO FLAVORANTS

| ALCOHOLS | ADDITIVE SMOKE FLAVOR |
|---|---|
| 2,3-Butanediol (T,TS) | Green, sweet, slight chemical off taste |
| **HYDROCARBONS** | |
| Styrene (TS) | Characteristic, styrax note at low concentration |
| **PHENOLS** | |
| 4-Ethylphenol (T,TS) | Sweet, musty, cellulosic |

Table 31.

## COCOA VOLATILES NOT PREVIOUSLY REPORTED AS TOBACCO FLAVORANTS

| ACIDS | ADDITIVE SMOKE FLAVOR |
|---|---|
| 4-Hydroxybenzoic Acid (T, TS) | Drying, some styrax type note |
| 2-Methoxybenzoic Acid (T) | Sweet, tobacco, flue-cured note |
| **KETONES** | |
| 2-Methyltetrahydrofuran-3-one (T) | Sweet, flue-cured like, adds body |

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COCOA Tables—from page 39

## MAJOR NON-VOLATILE ORGANIC ACIDS IN COCOA BEANS

| Acid | Ghana % | Bahia % | Sanchez % |
|---|---|---|---|
| Citric | 0.60 | 0.60 | 1.02 |
| Malic | 0.05 | 0.03 | 0.08 |
| Succinic | 0.04 | 0.05 | 0.02 |
| Oxalic | 0.39 | 0.39 | 0.24 |
| Lactic | 0.27 | 0.35 | 0.13 |
| Tartaric | (see note (3) below) | | |
| Gluconic | | | |

(1) Citric acid decreases, lactic increases on fermentation.
(2) Roasting of beans does not significantly change percentages.
(3) % not measured.

Table 32.

Table 33.

AMINO ACID COMPOSITION OF THE COCOA PROTEIN FRACTION

| Amino Acid | (g/100 g. Protein) |
|---|---|
| Isoleucine | 4.12 |
| Leucine | 7.46 |
| Lysine | 5.05 |
| Phenylalanine | 5.69 |
| Tyrosine | 3.76 |
| Cystine | 2.37 |
| Methionine | 1.50 |
| Threonine | 4.44 |
| Tryptophan (estimated) | 1.50 |
| Valine | 6.00 |
| Aspartic Acid | 9.12 |
| Glutamic Acid | 19.08 |
| Arginine | 5.77 |
| Histidine | 2.30 |
| Alanine | 5.79 |
| Glycocoll | 5.23 |
| Proline | 5.25 |
| Serine | 6.63 |

Table 34.

SMOKING EVALUATION OF SIMULATED COCOA AMINO ACID MIXTURE

| Ratio of Free Amino Acids In Cocoa* | | Smoking Evaluation of Synthetic Mixture** |
|---|---|---|
| Isoleucine | 5.0 | |
| Leucine | 14.3 | |
| Lysine | 7.1 | |
| Phenylalanine | 14.3 | |
| Tyrosine | 7.0 | |
| Cystine | - | |
| Methionine | - | |
| Threonine | 2.9 | Drying, adds body, harshness, enhances burley tobacco notes |
| Tryptophan | - | |
| Valine | 7.0 | |
| Aspartic Acid | 7.7 | |
| Glutamic Acid | 6.1 | |
| Arginine | 5.7 | |
| Histidine | 1.2 | |
| Alanine | 8.3 | |
| Proline | 4.8 | |
| Serine | 6.9 | |
| Glycine | 1.5 | |

* For flavor evaluation of individual amino acids see Leffingwell, Bernasek and Young, Tobacco Flavoring for Smoking Products (1972)

** Solubulized by pH adjustment with $NH_4OH$.