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IN TOBACCO SCIENCE

VOLUME 2

Leaf Composition and Physical Properties in Relation to Smoking Quality and Aroma

The 30th
Tobacco Chemists' Research Conference
1976
Nashville, Tennessee

NITROGEN COMPONENTS OF LEAF
AND THEIR RELATIONSHIP TO SMOKING QUALITY AND AROMA

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Introduction

Tobacco has been cultivated from a time that predates the discovery of the Americas (1). During this timespan, many changes in tobacco agriculture and curing practices have occurred, first through empirical discovery and, particularly in the last 40 years, through scientific agronomic research (2).

The genus *Nicotiana* has been used as a model phytochemical research organism in studies on plant virus, mineral nutrition, genetics, air pollution, and alkaloid metabolism. In fact, few plant materials have been more thoroughly studied than tobacco; but even so, only limited knowledge was generated prior to 1950 on the correlation of leaf chemical composition with smoking quality and aroma. The pioneering studies published in 1936 by Darkis and co-workers (3) on flue-cured tobacco stand as a landmark from which virtually all modern studies relating nitrogen constituents to quality have been launched. In this work, it was shown that for the better smoking grades of flue-cured tobacco, total sugar content was high, and α-amino nitrogen and total nitrogen were low, relative to grades of lesser quality. The Darkis relationships (Figures 1 and 2) of nitrogen components and sugars to both stalk position and leaf quality for flue-cured tobaccos are widely accepted. However, at that time, information on the role that sugars and nitrogenous compounds (with the exception of nicotine) play in the formation and transformation of chemical constituents contributing to the characteristic flavors and aromas in tobacco and other natural products was not available.

It has only been in the last decade that detailed leaf compositional studies on the volatile components in flue-cured [Roberts *et al.* (4-6)], burley [Roberts *et al.* (7), Demole *et al.* (8-12) and Kaneko *et al.* (13-15)] and oriental tobaccos [Enzell *et al.* (18-24), Schumacher (17), and Kaneko *et al.* (25-27)] have been published (28). Similarly, the composition of tobacco smoke (28) has been advanced tremendously in recent years, notably by the works of Schumacher (29-30),

FIGURE 1

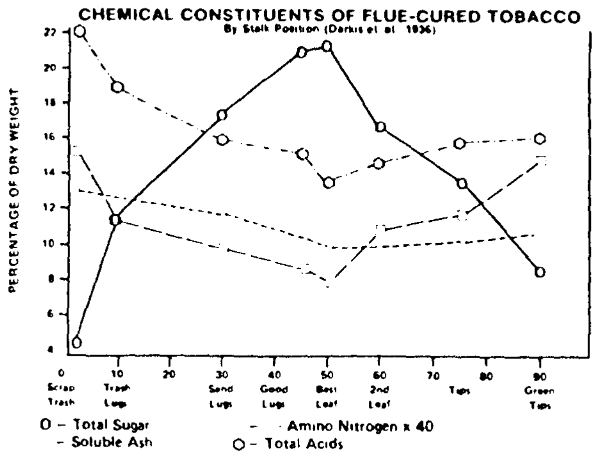
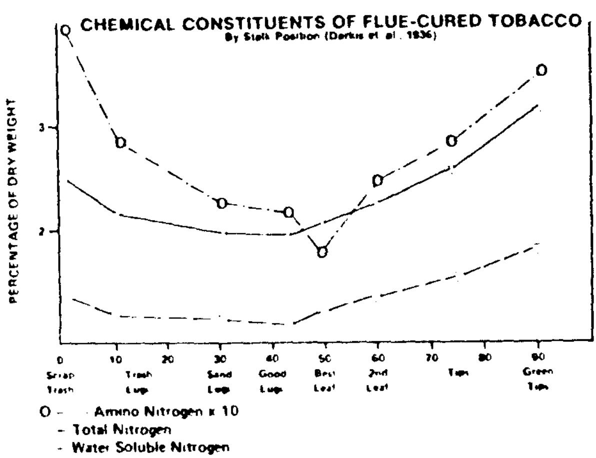


FIGURE 2



Grob (31-33), Novotny (34-35), Neurath (36-39), Elmenhorst (40-41) and others (42-71). In reviewing these extensive studies, one finds that a corollary exists between many of the identified volatiles of both leaf and smoke and similar compositional analyses in other flavorful natural product systems such as cocoa (73-79), tea (83), coffee (80-82), roasted nuts (84-87) and grains (88-90).

The attempt of this paper is to delineate the role that nitrogenous constituents in tobacco play in smoking quality and aroma. To this purpose it is necessary to touch briefly upon the major factors involved in the life cycle and subsequent treatment of the harvested leaf which determine both the gross chemical composition and quality before delving into the complex chemical transformations of nitrogen substances in the formation of natural tobacco and smoke flavorants.

Phytochemistry and Leaf Composition

The physical and chemical properties of leaf tobacco are influenced by genetics, agricultural practices, soil type and nutrients, weather conditions, plant disease, stalk position, harvesting and curing procedures. A change in any of these factors can markedly alter leaf composition and thus affect smoking quality (2).

It is now generally accepted that the metabolic carbon-nitrogen balance in living plants is due to continuing transformations based on the Krebs tricarboxylic acid cycle (2). In the Krebs cycle, carbon dioxide from air is assimilated through photosynthesis in the tobacco leaf while inorganic nitrogen (nitrate and/or ammonia) is assimilated through the roots from the soil. Soil nitrate is converted to ammonia which is utilized in the Krebs cycle to form amino acids which serve as a nitrogen pool for the formation and transformation of a multitude of nitrogenous chemicals important in the development of aroma and flavor quality. Dawson (91) has suggested a concept based on the Krebs cycle to account for inherited and culturally induced variations in gross tobacco composition. Using this concept, he rationally suggested that for tobaccos where the nitrogen supply is abundant, such as in cigar and burley tobacco production, there should be an abundant formation of protein, amino acids and nicotine. For oriental tobacco, where growth is maintained with limited supplies of nitrogen nutrients and water, there is an accumulation of acetate in the Krebs cycle resulting in the biosynthesis of terpenoids via mevalonic acid as well as a higher production of carbohydrates, "aromatic" acids, and resins at the expense of nitrogen constituents. Flue-cured tobacco is intermediate in that the phytochemistry during the plants life cycle is balanced by a moderate supply of nitrogen which is depleted as the plant reaches maturity.

Examination of representative analyses of the major cigarette tobacco types as presented by Harlan and Moseley (92) provides an overview of the major differences in aged flue-cured, burley, Maryland and oriental tobaccos. Although average reducing sugar content in flue-cured and oriental cigarette tobaccos today rarely runs as high as reported in Table 1, the basic analytical trends still remain valid. Thus, in air-cured burley, Maryland and cigar tobaccos the carbohydrates have been virtually depleted via metabolism of the living cells, whereas the protein and α-amino nitrogen are obviously higher than in flue-cured or oriental tobaccos. Conversely, the latter two tobaccos possess significant amounts of reducing sugars (which are absent in the former) and lesser amounts of protein and α-amino nitrogen.

Substantial changes in the chemical composition of tobacco leaf occur following harvest and during subsequent processes. This is illustrated by the data in Table 2 of Frankenburg (93) [as adapted by Tso (2)] for air-cured cigar tobacco which show the gross chemical changes in nitrogen compounds during curing. In general, there occurs some loss in total nitrogen, a reduction in insoluble protein via hydrolysis to amino acids, and formation of amino acid amides (as reflected by an increase in soluble nitrogen). Changes occurring in burley tobacco curing (94) are similar to those in stalk-cured cigar tobacco. In flue-cured tobacco, respiration in the primed leaf is arrested by the controlled dessicative dehydration during flue-curing which causes enzyme inactivation (2). Nevertheless, considerable change has occurred (Table 3) in the leaf (during the period after priming and early stages of curing) as starch loss occurs via enzymatic hydrolysis (95) with a concomitant increase in reducing sugar. It is important to remember that air-cured burley or cigar tobaccos before curing may contain 3-4% protein nitrogen, but flue-cured tobacco before curing contains only 15-20% of that amount.

TABLE 1

Representative analyses of cigarette tobaccos (leaf web after aging, moisture-free basis)

Component	Flue-cured Type 13	Burley Type 31	Maryland Type 32	Turkish[a]
Total volatile bases as ammonia, %	0.282	0.621	0.366	0.289
Nicotine, %	1.93	2.91	1.27	1.05
Ammonia, %	0.019	0.159	0.130	0.105
Glutamine as ammonia, %	0.033	0.035	0.041	0.020
Asparagine as ammonia, %	0.025	0.111	0.016	0.058
a Amiño nitrogen as ammonia, %	0.065	0.203	0.075	0.117
Protein nitrogen as ammonia, %	0.91	1.77	1.61	1.19
Nitrate nitrogen as NO_3, %	Trace	1.70	0.087	Trace
Total nitrogen as ammonia, %	1.97	3.96	2.80	2.65
pH	5.45	5.80	6.60	4.90
Total volatile acids as acetic acid, %	0.153	0.103	0.090	0.194
Formic acid,·%	0.059	0.027	0.022	0.079
Malic acid, %	2.83	6.75	2.43	3.87
Citric acid, %	0.78	8.22	2.98	1.03
Oxalic acid, %	0.81	3.04	2.79	3.16
Volatile oils, %	0.148	0.141	0.140	0.248
Alcohol-soluble resins, %	9.08	9.27	8.94	11.28
Reducing sugars as dextrose, %	22.09	0.21	0.21	12.39
Pectin as calcium pectate, %	6.19	9.91	12.14	6.77
Crude fiber, %	7.88	9.29	21.79	6.63
Ash, %-	10.81	24.53	21.98	14.78
Alkalinity of water-soluble ash[b]	15.9	36.2	36.9	22.5

a – Blend of Macedonia, Smyrna, and Samsun types.
b – Milliliters of 1 N acid per 100 g tobacco.

(Harlan and Moseley, 1955)

TABLE 2

Changes of nitrogenous compounds in air cured cigar tobacco
(% harvested dry weight)

Type of Nitrogen	Primed leaf: Before curing	Primed leaf: After curing	Stalk cured: Before curing	Stalk cured: After curing
Total	5.61	5.34	4.70	3.80
Protein (insoluble)	3.69	1.65	3.80	1.85
Soluble	1.92	3.69	0.90	1.95
Amino	0.23	0.80	0.15	0.15
Ammonia plus amide	0.15	1.07	0.05	0.80
Alkaloid	0.35	0.32	0.40	0.40
Nitrate	0.63	0.77	0.20	0.25
Remainder	0.56	0.73	0.10	0.35

(Frankenburg, 1946)

TABLE 3

Changes in composition of tobacco during the flue-curing process (% of dry weight)

Constituents	Green	Yellowed	Cured
Starch	29.30	12.40	5.52
Free reducing sugars	6.68	15.92	16.47
Levulose	2.87	7.06	7.06
Sucrose	1.73	5.22	7.30
Crude fiber	7.28	7.16	7.34
Total nitrogen	1.08	1.04	1.05
Protein nitrogen	0.65	0.56	0.51
Nicotine	1.10	1.02	0.97
Ash	9.23	9.24	9.25
Calcium	1.37	1.37	1.37
Oxalic acid	0.96	0.92	0.85
Citric acid	0.40	0.37	0.38
Malic acid	8.62	9.85	8.73
Resins	7.05	6.53	6.61
Pectinic acid	10.99	10.22	8.48
pH value	5.55	5.64	5.55

(Bacon, et. al., 1952)

In addition, in burley about 50% of the protein may undergo hydrolysis during air-curing while only about 20% of the protein is hydrolyzed in curing flue-cured tobaccos. Thus, burley tobacco possesses a relative abundance of free amino acids compared to flue-cured tobacco. Representative free amino acid analysis (Table 4) of high smoking quality blends of flue-cured and burley tobaccos with similar nicotine content selected from the 1972 crops illustrate this dramatically. In burley, we find the main free amino acids present to be aspartic acid, asparagine and glutamic acid, while for flue-cured proline, asparagine and glutamine are dominant. In total, 43 amino acids have been found in tobacco leaf (Table 5). Tso (2) in 1972 and Hamilton (94) reviewed the literature relevant to the changes which occur during curing and those interested in further aspects are referred to these sources. Suffice it to say that (1) genotype, (2) maturity, (3) stalk position, (4) harvesting practices and (5) curing practices are major factors relevant to the carbohydrate and protein hydrolysis changes that occur; *these chemical transformations are related to leaf quality.*

Cigarette tobaccos are almost never utilized in consumer products unless they have undergone a period of aging ranging from 12-60 months. Of course, inventory control is an important factor requiring maintenance of adequate stocks to allow periodic blend changes to occur; but, freshly cured and redried leaf is not used primarily because the smoke changes dramatically from a raw, somewhat irritating and disagreeable taste to a smoother, more rounded flavor during the aging process. Aging is ordinarily carried out at ambient temperatures and 8-12% moisture.

In areas with relatively long-term high ambient temperatures the desired aging effects are produced in shorter periods than in colder climates (97), and it is common for companies located in cold climate regions to store and age their tobaccos in southern locales. The role that nitrogen compounds play in the improvement of tobacco flavors with aging is important and the reasons for this will become apparent.

We shall now leave this brief discussion of the gross phytochemical and metabolic changes that occur in the leaf to discuss in somewhat more detail the role of nitrogenous substances in flavor

TABLE 4

REPRESENTATIVE FREE AMINO ACID ANALYSES

1972 Crop — High Quality Smoking Grade

(Blends)

Amino Acid	Flue-Cured (Mg/g.)	Burley (Mg/g.)
Aspartic Acid	0.13	7.84
Threonine	0.04	0.43
Serine	0.06	0.17
Asparagine	1.12	10.30
Glutamic Acid	0.10	1.78
Glutamine	0.82	0.38
Proline	4.11	0.45
Glycine	0.02	0.14
Alanine	0.32	0.35
Valine	0.06	(T)
Isoleucine	(–)	0.06
Leucine	(T)	0.10
Tyrosine	0.68	0.84
Phenylalanine	0.24	0.50
Lysine	0.03	0.33
Histidine	0.11	0.45
Arginine	(–)	0.26
Tryptophan	(–)	0.50

TABLE 5

AMINO ACIDS ISOLATED FROM TOBACCO

[illegible]-Alanine
[illegible]-Alanine
D-Alanylalanine
[illegible]-Aminoadipic Acid
[illegible]-Aminobutyric Acid
[illegible]-Aminobutyric Acid
Arginine
Asparagine
Aspartic Acid
Betaine
Choline
Citrulline
Cysteic Acid
Cysteine
Cystine

Glutamic Acid
[illegible]-L-Glutamyl-L-Glutamic Acid
Glutamine
Glutathione
Glycine
Histidine
Homocystine
Homoserine
Hydroxy Proline
Isoleucine
Leucine
Lysine
Methionine
Methionine Sulfone
1-Methylhistidine

Norleucine
Phenylalanine
Pipecolic Acid
Proline
Pyrrolidine-2-Acetic Acid
Serine
Taurine
Threonine
Tryptophan
Tyramine
Tyrosine
Valine
N-(3-Amino-3-
Carboxypropyl)-Nicotinic Acid

quality and the rather complex chemical transformations that occur in leaf during aging, processing and the smoking process.

<u>Nicotine and Flavor Quality</u>

This review would be incomplete without mentioning the role that tobacco alkaloids play in smoking quality. However, since nicotine represents the major component of this family and has been the subject of numerous publications, their role in smoking flavor will be touched on only by delineating the basic factors which are known to affect the flavor profile due to these substances.

It is assumed that nicotine is one of the primary satisfaction factors for which tobacco products are used. However, in air-cured tobaccos (cigar, burley, Maryland), the pH of the smoke is generally alkaline and the flavor effect of nicotine is a "harshness" which can be choking and unpleasant. In the case of tobaccos containing sugars (flue-cured, oriental), the tobacco is weakly acidic, the effect of nicotine is greatly modified, and the harshness is dramatically reduced. This same effect is often achieved by addition of sugars to air-cured tobaccos to "mellow" the smoke and/or by the blending of air-cured tobaccos with flue-cured and oriental (96). Thus, smoke pH and leaf sugar content are factors which play an important role in the nicotine strength perceived in the smoking process. But nicotine alone does not determine smoking flavor, or acceptability, as has sometimes been suggested by individuals unfamiliar with the flavor of various tobacco types.

<u>Nitrogen Compounds in Development of Tobacco Flavor</u>

Nitrogenous compounds in tobacco account for approximately 12-25% of the dry weight of freshly harvested tobacco leaves (98), (2-6% expresses as nitrogen). The major organic nitrogen constituents are nicotine and related alkaloids, proteins, and amino acids. As mentioned previously, the various methods of curing and aging cause only a small decrease in the total nitrogen content, but significant changes occur as a result of organic transformations from one type of nitrogenous compound to another; e.g., the enzymatic hydrolysis of leaf protein to free amino acids (94). After curing, dynamic changes continue to occur during aging, processing and smoking of tobacco leaf. Many of these are attributable to the chemical changes of, or induced by, nitrogen compounds - particularly the amino acids. This conclusion was reached by a number of workers including Weybrew, Woltz and Johnson (99) and Noguchi and co-workers (100) who recognized in 1965 that the transformations of amino acids could, and should, play an important role in the formation of tobacco flavor. Japanese workers have since contributed significantly to the literature by using model systems in which reactions of amino compounds with sugars or carbonyl compounds are shown to produce flavor compounds present in tobacco (101-106).

The corollary of the involvement of amino acids in desirable flavor formation in products such as cocoa is informative for illustration. Initially, in the case of cocoa beans (75), the raw material is allowed to undergo a mild natural fermentation to release reducing sugars, amino acids, phenolics, and flavonoids. The cocoa beans are then heat-cured to produce the full characteristic flavor through nonenzymatic browning reactions. Much of this flavor is due directly to the Maillard and Strecker reactions via the chemical interaction of amino acids with reducing sugars (or other carbonyls). The role of nonenzymatic browning reactions of amino acids and sugars is now generally accepted as being one of the most important processes in which natural flavors are produced. In the case of tobacco, browning reaction flavorants can be produced at any of several points: in the dynamics of curing, during aging of leaf and its processing, or during the smoking process. This is not to imply that other flavor-producing processes, such as the oxidative degradation of terpenoids and carotenoids, are not important, but these relationships to quality will be discussed by others in this symposium. Suffice it to say that at least the following flavor-forming mechanisms appear operative in the tobacco leaf:

I. Enzymatic hydrolyses
II. Oxidative transformations (enzymatic or other)
III. Ambient temperature nonenzymatic transformations
IV. Heat induced nonenzymatic transformations

It must be remembered that compounds formed by enzymatic processes can react subsequently in a nonenzymatic transformation. It is useful at this point to examine several examples of each type of transformation.

First, enzymatic transformations which provide the building blocks for the formation of browning reaction flavors are represented by the hydrolysis (Figure 3) of proteins to amino acids and of starches to free reducing sugars in freshly harvested leaf (2).

Oxidative transformations (Figure 4) may be enzyme catalyzed, microbiological or chemical in nature and can be represented by (a) the oxidative deamination of amino acids to ammonia, carbon dioxide and carbonyl compounds (108), (b) the conversion of nicotine to 6-hydroxy-nicotine, nicotinic acid and other pyridine derivatives (107), (c) the oxidative degradation of sugars to acids and other carbonyl compounds (108), and (d) the conversion of lipid materials to carbonyls (109).

Unfortunately, for this discussion, many carbonyl constituents present in tobacco leaf which can, and do, undergo further transformations may arise by several different pathways. A simple example (Figure 5) is the multiple routes possible for the formation of propanal. Nevertheless, amino acids derived from leaf provide several potential routes to many of the flavorful carbonyl compounds and reactants involved in further transformations involving nitrogen. It is quite possible (and even probable) that different tobaccos and curing methods involve different mechanisms for the formation of the same isolated constituents.

By examining the chemical transformations involved in the production of nonenzymatic browning reaction flavorants one finds several routes which can be involved in the production of the same flavorants from different precursors.

Nonenzymatic Browning Reaction Flavors

In view of the compelling evidence, a large variety of flavor compounds present in tobacco and smoke must be presumed to be derived from the amino acids, sugars, carbonyl compounds, ammonia and chemical transformations thereof.

In the case of tobacco leaf containing both amino acids and reducing sugars, as is notably the case in Virginia or flue-cured leaf, it has been shown by Noguchi and co-workers (100, 110-113) that amino acids react directly with reducing sugars in leaf to form isolable Amadori compounds (amino acid-sugar compounds)(Table 6)which may constitute as much as 2% of the dry tobacco weight (98). The major Amadori compounds have been shown (Figure 6) to go through an initial

FIGURE 3

ENZYME HYDROLYSES

Protein(s) ⟶ Amino Acids

Starches ⟶ Reducing Sugars

FIGURE 4

ENZYMATIC REDOX REACTIONS

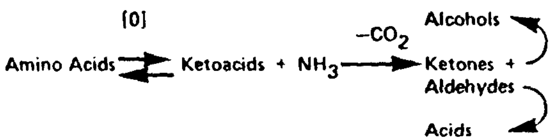
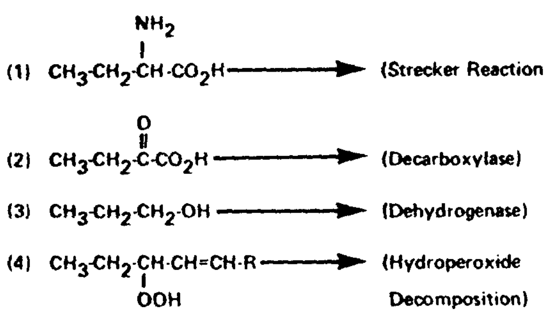


FIGURE 5

POTENTIAL PRECURSORS OF PROPANAL



(5) Stepwise Oxidation of Higher n-Aldehydes

TABLE 6

AMADORI COMPOUNDS FOUND IN FLUE-CURED TOBACCO

1-Deoxy-1-L-Prolino-D-Fructose

1-Deoxy-1-L-Alanino-D-Fructose

1-Deoxy-1-L-Valino-D-Fructose

1-Deoxy-1-L-Threonino-D-Fructose

1-Deoxy-1-L-Phenylalanino-D-Fructose

1-Deoxy-1-L-Tyrosino-D-Fructose

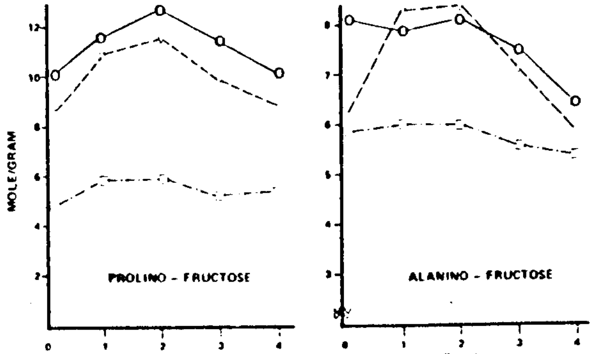
1-Deoxy-1-(N-ε-Aminobutyric Acid)-D-Fructose

1-Deoxy-1-Aspargino-D-Fructose

FIGURE 6

CHANGES IN AMADORI COMPOUNDS IN FLUE-CURED TOBACCO ON AGING

(Noguchi et al., 1971)



O - 1st Grade Leaf (Miyazaki)
∇ - 1st Grade Leaf (Kurashiki)
- 3rd Grade Cutter

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increase and then a gradual decrease over a four-year aging study (111). The dynamics of having free amino acids, free reducing sugars, and Amadori compounds present in flue-cured leaf, and the isolation of flavorants derivable via the Maillard decomposition reaction of these, suggest that at least part of the improvement in flue-cured leaf quality is related to this reaction. Chemically, three pathways of the Maillard reaction have been defined, two of which initially involve reducing sugars. Of particular importance is the fact that reducing sugars can be transformed to other carbonyl compounds at relatively low temperatures in the presence of amino compounds, and two pathways (Figure 7) of the Maillard Reaction directly involve reducing sugars. The amine function involved may be an amino acid, an amine, or free ammonia derived by deamination of amino acids. Since all three of these classes are present, multiple reactions are undoubtedly occurring.

A third pathway of the Maillard reaction which requires the presence of active alpha-dicarbonyl components (which may originate either enzymatically or nonenzymatically) is the Strecker degradation of α-amino acids to aldehydes and ketones of one less carbon atom. The mechanism of the Strecker degradation involving pyruvaldehyde and α-alanine is shown according to Schonberg and Moubacher (114-115) along with its significance in the formation of the important 2,5-dimethylpyrazine and 2,5-dimethyl-3-ethyl pyrazine (Figure 8), two of the major reaction products of the self-condensation of amino-acetone (116). The fact that different amino acids can produce the same flavor compounds has been shown by a number of workers in studies on the relative formation of pyrazines under controlled reaction conditions between amino acids-glucose (105, 106, 118). Similar studies have shown that thermal decompositions of various amino acids and other aminohydroxy compounds such as glucosylamine can directly form pyrazine mixtures (119). Unfortunately, very little has been published on the pyrolysis of these materials in a manner designed to simulate the dynamics of cigarette smoking (120).

Because of the complexity of the chemical interactions and transformations involved, the types and ratios of active flavor products formed by nonenzymatic browning are dependent on the reaction conditions which may occur during aging or during the smoking process itself. Let us now review some representative flavorants (Table 7) known to be produced by nonenzymatic browning and which occur either

FIGURE 7

TWO PATHWAYS OF REDUCING SUGARS IN THE MAILLARD REACTION

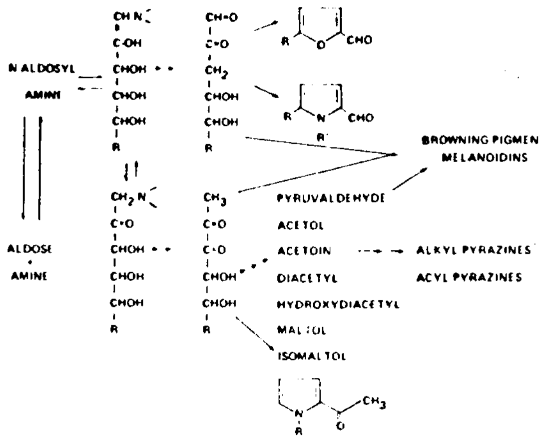


FIGURE 8

THE STRECKER REACTION → MAILLARD REACTION

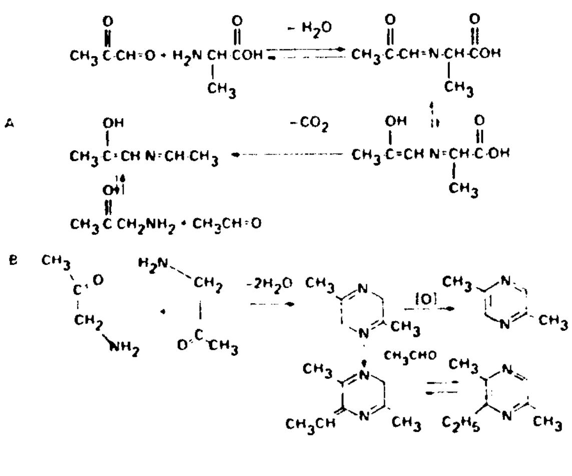


TABLE 7

SOME BROWNING REACTION PRODUCTS OF AMINO ACIDS (OR AMMONIA) AND SUGARS PRESENT IN TOBACCO AND/OR SMOKE

Acids	Additive Smoke Flavor
Acetic (T,S)	Pungent, Acrid
Propionic (T,S)	Pungent, Acrid
Butyric (T,S)	Smoothing, Buttery, Fruity
Isovaleric (T,S)	Sweet, Winey, Turkish

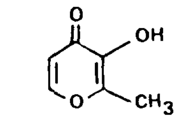
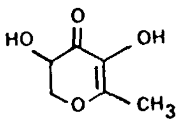
Aldehydes	Additive Smoke Flavor
Acetaldehyde (T,S)	Pungent, Acrid, Weak Fruity
Propionaldehyde (T,S)	Pungent, Nutty
Butyraldehyde (T,S)	Harsh, Green
Isobutyraldehyde (T,S)	Sweet, Chocolate, Nutty
n-Valeraldehyde (T,S)	Chocolate, Fruity
Isovaleraldehyde (T,S)	Chocolate, Nutty-Buttery
2-Methylbutanal (T,S)	Chocolate, Burley
n-Hexanal (T,S)	Spicy, Green-Apple
2-Methyl Pentanal (S)	–
n-Decanal (T)	Green, Citrus
Acrolein (T,S)	–
Crotonaldehyde (T,S)	–
Phenylacetaldehyde (T)	Floral (Rose)
Benzaldehyde (T,S)	Almond, Cherry, Sweet
Pyruvaldehyde (T,S)	Adds Body, Sweet, Caramel

TABLE 7 (cont.)

Ketones	Additive Smoke Flavor
Acetone (T,S)	–
2-Butanone (T,S)	Sweet, Ketonic
2-Pentanone (T,S)	Ketonic, Fruity, Sweet
2-Hexanone (S)	–
4-Heptanone (S)	Sweet, Fruity, Green
2-Heptanone (T)	Sweet, Fruity
Acetol (T,S)	Smoothing, Winey
Acetoin (S)	Sweet, Buttery
Diacetyl (T,S)	Buttery, Sweet
Pentane-2, 3-Dione (S)	Buttery
Acetophenone (T,S)	Sweet, Ketonic (Cherry-Hay)
Methyl Cyclopentenolone (T,S)	Sweet, Caramel-Maple

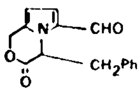
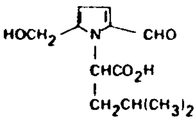
Furans	Additive Smoke Flavor
Furan (S)	–
Furfural (T,S)	Sweet, Yeasty-Bread, Buttery
Furoic Acid (T,S)	Weak Sweet, Nutty
Furfuryl Alcohol (T,S)	Cereal-Like, Bran, Oily
Furfuryl Acetate (S)	Herbaceous, Spicy
2-Acetylfuran (T,S)	Green, Herbaceous
5-Hydroxymethylfurfural (T,S)	Sweet, Floral, Flue-Cured Note
2,5-Dimethylfuran (S)	–
5-Methyl-2-Acetylfuran (T,S)	Sweet, Aromatic, Spicy Enhanced Burley Note
5-Methylfurfural (T,S)	Sweet, Adds Body
Isomaltol (T,S)	Roasted, Caramel

TABLE 7 (cont.)

Pyrans		Additive Smoke Flavor
 (Maltol)	(T)	Sweet, Flue-Cured Like
	(S)	Sweet, Flue-Cured Like

Pyrazines	Additive Smoke Flavor
2-Acetyl Pyrazine (T)	Buttery-Nutty (Popcorn)
2-Acetyl-6-Methyl Pyrazine (T)	Buttery-Nutty (Popcorn)
2-Acetyl-3-Methyl Pyrazine (T)	–
2-Methylpyrazine (T,S)	Dull, Sweet, Aromatic
2,3-Dimethyl Pyrazine (T,S)	Bread-Like, Roasted
2,3,5-Trimethylpyrazine (T,S)	Burley Character, Sweet
2,3,5,6-Tetramethyl Pyrazine (T,S)	Burley Note
2,5-Dimethyl Pyrazine (T,S)	Earthy, Pleasant
2,6-Dimethyl Pyrazine (T,S)	Dull Herbal Sweetness
2-Ethylpyrazine (S)	Earthy
2-Ethyl-6-Methylpyrazine (T,S)	Dry, Sweet, Resinous
2-Ethyl-5-Methylpyrazine (T,S)	Mellowing
2,5-Dimethyl-3-Ethyl Pyrazine (T,S)	Burley Note
2,3-Dimethyl-5-Ethyl Pyrazine (T,S)	–

TABLE 7 (cont.).

Pyrroles		Additive Smoke Flavor
N-Methyl 2-Formylpyrrole (T,S)		Sweet, Cherry, Adds Body
5-Methyl-2-Formyl-Pyrrole (T,S)		Cherry, Adds Body
2-Formyl Pyrrole (T,S)		Sweet, Smoothing
2-Acetyl 5-Methyl Pyrrole (T,S)		Sweet, Cherry
2-Acetyl Pyrrole (T,S)		Floral, Green, Winey
	(T)	Hot, Peppery
	(T)	Smooth, Sweet Nutty

Miscellaneous	Additive Smoke Flavor
Pyridine (T,S)	Sweet, Flue-Cured
2-Methylpyridine (S)	Burley Character
3-Methylpyridine (S)	Burley Character

in tobacco (T) or smoke (S).

In addition to the expected aldehydes, ketones, pyrazines, pyrans, furans, and simple pyrroles formed by the Strecker and Maillard reactions, it is significant that several 1-alkylacid-2-formyl-5-hydroxymethylpyrroles and 2-(5-hydroxymethyl-2-formylpyrrol-1-yl) alkyl acid lactones found in flue-cured tobacco have been isolated from roasting alkyl amino acids with D-glucose (5, 104).

Tobacco Processing

The implication of nonenzymatic browning reactions during tobacco processing has been shown by Bright, Larson and Lewis (117) who demonstrated that the weight percentages of five amino acids were significantly reduced by heat treatment, while the pyrazine content increased dramatically under conditions where percent of nicotine remained constant (Tables 8 and 9). Thus, it is quite likely that the highly secret, but usually empirical, procedures used by each manufacturer in processing tobacco blends can contribute to the development of specific flavor characteristics.

Summary

The browning reactions which can occur during the curing, processing and smoking process and which involve nitrogen compounds must be considered as contributing significantly to the flavor and aroma perception of tobacco and, as more sophisticated research is carried out, it is conceivable that lower quality tobacco grades may possibly be upgraded by either enzymatic, heat or chemical processing under controlled conditions to improve flavor quality. The recent plethora of patents on the use of browning reaction products as flavorant additives indicates that this area of research is active in the tobacco industry (121). Finally, preliminary studies indicate that in flue-cured tobacco at least two amino acids (alanine and glutamine) may directly correlate (Table 10) to smoking quality as indicated by high negative correlation coefficients (122).

TABLE 8

CHANGE IN AMINO ACID LEVELS ON TOBACCO AFTER ROASTING

(Complete Cigarette Blend)

	Before % (W)	After % (W)	Δ %
Aspartic Acid	1.39	0.82	− 41
Proline	0.65	0.31	− 52
Lysine	.32	0.10	− 69
Histidine	.24	0.16	− 33
Arginine	.16	0.06	− 62

(Bright, et. al. 1975)

TABLE 9

EFFECTS OF ROASTING ON DIMETHYLPYRAZINE CONCENTRATION

	Conc. Prior To Roasting (ppb)	Conc. After Roasting (ppb)
Flue-Cured or Bright	0.1	0.3
Turkish	0.1	0.3
Burley	0.1	460
Reconstituted Leaf	0.1	200

Tobacco Samples Were Shredded, Without Additives
Roasted 4 Hours At 120 · 3° C

(Bright, et. al. 1975)

TABLE 10

SMOKING QUALITY CORRELTION COEFFICIENTS OF SEVEN COMPOSITE FLUE-CURED GRADE BLENDS*

	Aroma	Flavor	Mildness	Overall Opinion	Glutamine
1. Aroma	1.0000				
2. Flavor	.8714	1.0000			
3. Mildness	.8334	.7653	1.0000		
4. Overall Opinion	.8644	.9571	.6171	1.000	
5. Glutamine	−.8612	−.8374	−.7702	−.8553	1.0000
6. Alanine	−.8904	−.9111	−.7665	−.9208	.9822

*1972 Crop: Quality Range From Poor To Very Good.

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