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COMPOSITION OF TOBACCO RELATED TO SMOKING CHARACTERISTICS

Importance of Nicotine

The earliest analysis of all types of tobacco grown in the United States was made by Dr. F. B. Carpenter (4) at the North Carolina Experiment Station in 1895. His analyses showed the marked difference in the level of nitrogenous constituents between flue-cured and air-cured types of tobacco. This work was done before the significance of sugars in flue-cured tobacco was recognized and Dr. Carpenter did not include this class of compounds in his determinations. His interpretation of results was necessarily restricted by the limited state of the knowledge at that time. With respect to nicotine, however, he made the following comment: "Best are considered the best qualities, almost always contain a small percentage, while a large percentage usually indicates coarseness".

It is worthy of note that the cultural practices of his day were quite different from those which later came into vogue after cigarette smoking created a demand for a milder tobacco, that is one containing less nicotine. Nevertheless, the adverse effect of high nicotine content upon quality was apparent, even at that time. It is significant that among cultural changes was closer setting, and high, or no topping. Dr. Garner discovered that the practice of low topping (that is, cutting back the tobacco plant at the time of flowering) materially increased the nicotine content and the body of the leaf. This was confirmed by Dr. Haley (13) of the Pennsylvania State College, and by the New York Agricultural Experiment Station (19).

A wealth of information on tobacco culture has issued from the investigations directed by Dr. Garner, who may appropriately be called the dean of American authorities on tobacco. During a long and productive career he has been associated with the Bureau of Plant Industry of the U.S.D.A., first as Scientific Assistant and finally as Principal Physiologist, in charge, Division of Tobacco and Plant Nutrition.

In 1909 (9) he published a paper on "The Relation of Nicotine to Quality of Tobacco". We now know, as Dr. Garner stated at that early date, albeit the fact was frequently overlooked by less qualified investigators who followed him, that "although nicotine is the active principle of tobacco...the finest grades...contain only moderate (and even relatively small) amounts of this principle"

Dr. Garner considered the term "strength" as a composite made up of two factors: one, the true physiological action of nicotine commonly spoken of as "fullness", the other, the "pungent, burning quality" which is the antithesis of "smoothness". He discovered that the nicotine existed in at least two forms in tobacco, one free, the other fixed. He ascribed the harshness of smoke to the presence of the free nicotine.

The gist of Dr. Garner's observations is indicated by quotations from his Conclusions: "...a distinction must be drawn between two forms of nicotine contained in tobacco, one of which is easily volatile...while the other is volatile only at elevated temperatures. The undesirable sharpness or pungency contained in the smoke from certain types of cigar filler tobacco...is due almost entirely to the volatile, easily soluble form of nicotine which acts as if it were in the free state. The pungent, harsh quality of the smoke is partially, but not entirely removed by a protracted re-sweating and aging of the tobacco, whereby the easily volatile nicotine is largely expelled. This undesirable property is entirely removed by extracting the tobacco with petroleum ether, which simply dissolves out the volatile nicotine". Nothing has since been discovered to contravene these early observations of Dr. Garner with respect to "free" nicotine.

In 1954 (11) Dr. Garner reported the results of fertilization studies on Maryland tobacco, embracing a period of over ten years. He pointed out that Maryland cigarette

tobacco was characterized by a relatively low nitrogen content and stated: "It is also characterized by a relatively low nicotine content to which it owes its mildness".

Dr. Garner also recognized and commented upon the influence of soil, rainfall, position on the stalk, and factors other than seed and fertilization, upon the content of nicotine and other constituents, resulting in wide variation in crops and even in composition of individual leaves. This explains the need of careful selection in the purchase of cigarette tobaccos.

Dr. Garner also called attention to the fundamental differences between the various types of cigarette tobaccos which make them "mutually supplemental" for blending purposes.

Curing Effects

The differences in chemical composition of tobaccos and their suitability for blending cannot readily be understood without a knowledge of the curing processes. Dr. Garner (10) engaged in a study of air curing reactions and reported his findings in 1914. Although his investigation was confined to cigar tobaccos, we have found in this laboratory that the changes which he observed are strictly analogous to those which take place in the air curing of Burley. Essentially, he describes curing as a living process in which the plant strives to prolong its life at the expense of food in the form of starches and sugars which have been stored up during growth. The alteration in the chemical composition of the leaf is extensive. Dr. Garner describes some of the fundamental changes involved in air curing:

All starches and reducing sugars disappear

Pentosans decrease

Malic acid decreases

Citric acid increases

Protein decreases up to 60% of the original

Nicotine and total nitrogen decrease

Ammonia is formed

The entire process appears to be one of chemical simplification. The starches are converted into sugars, thence into the fixed acids, malic and citric; these are in turn broken down, in part, into simpler more volatile compounds, although some of them remain in the cured leaf.

The nitrogenous constituents pass through like stages of degradation. Proteins which are stable and insoluble nitrogenous compounds of complicated structure are, in large measure, converted into amides which are of simpler structure and in the words of Dr. Garner "...cleavage products of protein are further changed, with ammonia as one of the decomposition products. The observed increase in the content of ammonia, therefore, represents only a portion of the total quantity formed during the curing, the amount which becomes fixed in the leaf doubtless depending on the quantity of free acid present".

Long before the work of Dr. Garner, two European investigators, Muller-Thurgau (18) (1895) and Behrens (1) (1894) had observed the disappearance of starch and a decrease of sugar during the curing process. Behrens had noted the decrease in protein nitrogen.

Pursuing further the work of Dr. Garner, Vickery and Pucher at the Connecticut Agricultural Experiment Station published (1931-1935) a series of bulletins on air curing, entitled "Chemical Investigations of the Tobacco Plant". They made an

exhaustive quantitative study of both the acid decomposition products of the starches and sugars, and of the less stable basic compounds formed by decomposition of protein material. Their research consisted of an elaboration of principles previously enunciated by Dr. Garner.

With reference to flue curing, as compared with air curing, Dr. Garner (10) stated: "In the case of flue curing where much higher temperatures are used, no comprehensive investigations have been made; but analyses of the cured leaves which have been reported show that the curing changes are of the same character as in air curing, the only difference being that in flue curing the transformations are less complete".

No investigation of flue curing on a scale undertaken for air curing by Dr. Garner has ever been made outside of this laboratory. We have followed chemical changes through the successive stages in the processing of flue-cured tobacco from the field to the market. The primary changes are the accumulation of large amounts of sugars at the expense of starches which practically disappear, and the reduction of protein material which is replaced by less stable forms of nitrogenous compounds. The essential difference between flue and air curing is, as Dr. Garner predicted, in degree. The flue curing process terminates the life of the plant at an early stage in the cycle of changes so that the sugars remain intact instead of suffering decomposition as in air curing.

Aging Reactions

The picture of chemical composition of cigarette tobaccos is incomplete without a consideration of aging, which always precedes blending and manufacturing. During the periodic "sweats", to use a word employed by the experienced tobacco manipulator

to describe the behavior of stored tobacco during the spring and fall, the leaf heats, darkens, develops aroma, becomes more combustible, less harsh, and more pleasing when smoked. The reaction changes are clearly the results of oxidation.

The reactions during the aging of flue-cured tobaccos were studied extensively by Gross and associates (5) at Duke University during the years 1928 to 1935, and their observations were reported in 1935. In addition to the observed improvement in aroma and smoking quality, which is the practical reason for subjecting tobacco to aging, they observed a number of definite chemical effects. Practically all of the constituents determined registered a decrease. These included among the acid producing components, sugars and non-volatile acids; among the base producing constituents, total, soluble and alpha-amino nitrogen. There was a degradation of all of these constituents, presumably by oxidation into simpler compounds which escaped into the atmosphere or remained absorbed in the leaf. Nicotine diminished, probably by volatilization of the free bases.

As evidence of the nature of these reactions, the authors identified acetic and formic acids, acetaldehyde and ammonia in the atmosphere surrounding the aging tobacco. However, they omitted the quantitative determination, in the tobacco, of some of the most important of these end-products.

In this laboratory, the aging reactions of flue-cured tobaccos have been followed in two successive crops over a three-year period. One of the most striking effects discovered was the proportionally large increase in volatile acids in which formic and acetic were identified. This is the most definite and characteristic of all aging reactions. These acids must be considered as by-products of the main reactions of aging in which aroma is developed and combustion improved. They certainly do not contribute to the mellowness of the tobacco, but, to the extent in which they accumulate

in the leaf, are a detriment to this desirable quality. The same reasoning holds for the aldehydes.

The aging of air-cured tobacco, so far as we know, has not been studied except in this laboratory. In the production of volatile acids, the reactions are similar in both flue curing and air curing processes. The increase is of the order of 70 to 80%. This is by far the greatest proportional change which any constituent, or group of constituents undergoes during aging.

Unlike flue-cured, the air-cured type shows a definite increase in ammonia and other volatile bases and an accumulation of these compounds in the leaf. This class of constituents may be considered as another objectionable by-product of the otherwise beneficial aging reactions.

The fundamental differences in chemical composition of air and flue-cured tobaccos lead to the prediction that the former would yield predominantly basic, the latter predominantly acidic constituents in the smoke. This is precisely what is found when Burley or Bright is smoked straight, that is without blending. Although the curing and aging reactions of both have much in common, each is characteristic of its type. The antagonistic or "mutually supplemental" nature of the two types offers a scientific explanation for the success of their blending, the merits of which were discovered empirically long before science had developed sufficient information to suggest a reason for the practice.

It is an interesting fact that the processes of curing and aging give rise to end-products which are in part easily identified, are volatile, and are known to be irritating.

Chemical Evaluation

In this country, after Dr. Garner's early discovery of the irritating properties of free nicotine, little effort was made to correlate composition of tobacco with smoking quality. The U.S.D.A. and State experimental stations were engrossed in the more practical problems of improving the physical quality of tobacco, increasing yields, and combating disease. At the Connecticut Agricultural Experiment Station, Vickery's investigations, though extensive, were concerned with plant physiology and the chemistry of cell structure. They were not related to quality of tobacco or its use.

Government and State tobacco specialists relied upon the keen judgment of the expert buyer to determine the desired quality and he, in turn, was equally sensitive to popular acceptance of his product. As the result primarily of popular demand, both agronomist and manufacturer were seeking a lighter bodied, milder smoking tobacco, without having adequately defined lighter body or mildness except by the recognition of certain physical characteristics associated, in experience, with mildness. Nevertheless, the effect on cultural practices and other controllable factors was approximately the same as if it had been the product of design, based on a scientific study and definition of mildness.

It was instinctively recognized that judgment of quality was governed by the manufacturing purpose for which tobacco was purchased. For example, a wrapper tobacco of the finest quality might be of quite inferior value for a cigarette blend. Cigarette tobaccos were bought for blending with other tobaccos of known smoking characteristics and judgment of their value was determined by this consideration. With the exception of nicotine, the factors of chemical composition which determined the suitability of tobaccos for cigarette blending were, for the most part, ignored.

That there was a tendency to produce tobacco of lower nicotine content, perhaps not entirely deliberately, is evidenced by the continuing trend toward a lower nicotine content in tobacco and tobacco products. Other factors of importance did not receive the attention of those who were capable of, or equipped to evaluate them.

In Europe, the situation was quite different. The tobacco industry was, for the most part, a state monopoly. The public did not need to be considered, although their tobacco products, according to American standards, were very inferior. Possibly a recognition of this inferiority stimulated the type of research which lagged, at least among official agencies, in this country. Whatever the impetus, numerous foreign investigators attempted the chemical evaluation of tobacco in relation to smoking quality.

Importance of Acid and Base Producing Constituents

One of the earliest students of the problem was Professor K. B. Lehmann(17) University of Wurzburg, who reported his findings in 1909. Lehmann did not develop a basis for the chemical evaluation of tobacco, but he discovered the principle of acid-alkaline balance. He compared the smoke of tobacco and a plant tissue described as Spanish reed and observed that the latter produced a much more acidic type of smoke. That he took cognizance of the effect of acidic type of irritation is indicated by his statement: "No wonder that the smoke of the Spanish reed is so acid that it bites the lips and gives a distinct acid taste."

In Russia, there was established in 1917 a state institute of tobacco research. This was continued under several successive five-year plans and embraced all phases of tobacco culture and manufacturing. Under the direction of Professor A. S. Simuk,

about a hundred voluminous bulletins have been released at intervals by this institute. Shmuk attempted to devise a formula for the evaluation of tobacco, which later became known as the "Shmuk number". This was represented by the ratio of carbohydrates to nitrogenous constituents in the tobacco, and considered in terms of the products of the smoke of these two classes of compounds is essentially an acid-base relationship. Although he considered an increase in carbohydrate or acid forming constituents favorable to quality, he recognized the possibility of having an excess of this class of compounds, for he stated (22): "An acid smoke gives not so much a strong as a sharp and sometimes a slightly burning taste."

In 1930, Faitelowits (6) employed a ratio of acids over bases in evaluating mildness of tobacco. According to his formula, the acids denoted the acidity of the tobacco and the bases the alkalinity of the smoke from the burning tip of the cigarette.

In the same year, Gabel and Kiprisnov (7) observed that the higher qualities of tobacco yielded more acids in the smoke.

In 1931, Gawrilow and Koparina (12) observed that by adding carbohydrates to tobacco, a decrease in the nicotine and ammonia content of the smoke occurred. This was considered a favorable reaction.

In 1935, P. Koenig (15), in an address on light and heavy bodied tobaccos, enumerated the constituents which were favorable and unfavorable to smoking quality. He designated protein as favorable if sufficient sugar was present, but he considered high protein combined with low sugar and carbohydrate content as detrimental. He very definitely recognized the relation between acid forming and base forming constituents of tobacco and appreciated the fact that one supplements the other.

In the same year, Hall and Earl (14) reported the results of preliminary investigations, during which they noted that poor tobacco gave unpleasant odors suggestive of lower amines (bases). They also stated that the smoke from good tobaccos was slightly acidic or neutral, while that from poor tobacco was usually definitely alkaline. They concluded that the presence of acids in the leaf and production of acid during combustion tended to hold the bases combined as salts.

At about the same time, John E. Symons (25) in Canada compared his native tobacco with American types and observed that the nicotine decreased with increasing quality, while the sugars increased.

In 1938, H. Bruckner (3) published a handbook on tobacco and tobacco smoke. He clearly recognized the relation between acid producing and base producing constituents of tobacco. Among the constituents giving strength, he included total nitrogen, protein nitrogen, and nicotine. Among those producing mildness, he listed sugar, starch and oxalic acid. He goes further, however, and states that if the constituents producing "mildness" are present in excessive amounts, and he includes here carbohydrates other than sugar and starch which form the cell membrane, not mildness but sharpness results.

In 1957, Kieser (21) investigated Turkish tobacco for the purpose of finding some simple means of chemical evaluation. He stated that nicotine, protein compounds, and their decomposition products, made tobacco strong and caused the irritation in the throat. He observed that, in general, mineral matter decreased quality and expressed mildness as the ratio between soluble carbohydrates and ash. (It may be noted that in the type of tobacco which he investigated, higher ash is invariably associated with higher nitrogenous constituents. In effect, therefore, his formula for mildness

becomes a ratio between soluble carbohydrates and nitrogenous constituents.)

He made the interesting observation that carbohydrates yield acids which neutralize bases in the smoke and thus decrease its strength. His comments on reactions to smoking Smyrna tobaccos, which as a result of plant breeding were devoid of nicotine content, are significant. He reported that they exhibited a corrosive, sharp taste never found in normal tobaccos, which approached that of burning cellulose or dried grasses. (This is an instance in which, by breeding, the base forming constituents were evidently reduced to a point where acid producing constituents in the smoke predominated, yielding smoke which was irritating due to acids and related constituents.)

In 1939 Shmuk (22) presented an analysis of tobaccos of different grades and stated: "Table III shows clearly that alkalinity of smoke definitely increases in passing from high to low grade tobaccos".

In the same year, Gaertner (8), who investigated Hungarian tobaccos, evaluated strength of tobacco in terms of nicotine, protein nitrogen and total nitrogen. He expressed mildness as a ratio between soluble carbohydrates and the ash.

In 1940, Bodnar and Votinsky (2) reported the results of determining the bases generated in smoking tobacco and obtained a numerical evaluation of quality. According to their method, the lower the bases in the smoke, the better the quality of the tobacco.

The observations reported by the above quoted investigators were based on a correlation between the reactions of experienced smokers and the analysis of tobacco or the smoke. It is the consensus of opinion that, at the present time, this is the only manner in which tobacco can be intelligently evaluated. It should be borne in mind that most of these tobacco specialists were limited in their scope of investigation to the darker, more alkaline types of tobacco. It was natural that they should

observe an improvement in the quality of the smoke when the acid forming constituents of this type of tobacco were increased. It is particularly interesting that several of them found that this kind of improvement could be carried too far, resulting in an overbalancing of the base forming constituents and the production of an excessive amount of acids in the smoke. In general, they recognized that nicotine and other smoke bases were responsible for strength, harshness and pungency, but that the antithesis of these, the acids, likewise produced irritation.

The principle of acid-base balance, recognized and enunciated by these investigators, is in complete accord with the results of research conducted in this laboratory, which has formed the basis for the scientific control of selection, blending and processing of tobaccos.

Resins

Considerable attention was devoted to a study of the significance of the resin content of tobaccos in relation to quality. This is of interest since the resins are transmitted to the smoke and comprise a part of the fraction usually designated as "tars and resins".

Bruckner found a direct relationship between the resin content of cigarettes and their price. Koperina (16) recovered the resins from tobacco which was burned in a retort. He observed that the higher qualities of tobacco yielded more resins.

Wenusch (24) and Pyriki (20) were for years engaged in investigations of tobacco and tobacco smoke, the former in Austria, the latter in Germany. Wenusch isolated and identified resins in the smoke of Oriental tobaccos and he found that the so-called tar in the smoke retained the original resinous character of these constituents in the tobacco. Pyriki established the fact that about 75% of the resins in the

tobacco were transmitted to the smoke with little change in characteristics.

Gaertner (8) considered the aroma to be due to the resins and polyphenols in the tobacco.

References

(1) Behrens, J.
Further Contributions to the Knowledge of the Tobacco Plant
Landw. Vers. Sta. 45, 271-301 (1896)

(2) Bodnar, J. and Z. Votinsky
Evaluation of Tobacco on the Basis of Chemical Composition and the Determination of Quality through the Reaction of Tobacco Smoke or through the Smoke Number
Z. Untersuch Lebensm. 80, 515-527 (1940)

(3) Bruckner, H.
Die Biochemie des Tabaks (Biochemistry of Tobacco)
Paul Parey, Berlin, 1938, 446 pages

(4) Carpenter, F. B.
Types of Tobacco and Their Analyses
North Carolina Agricultural Experiment Station, Bulletin 122 (1895)

(5) Dixon, L. F., F. R. Darkis, F. A. Wolf, J. A. Hall, E. P. Jones and F. M. Gross
Flue Cured Tobacco - Natural Aging of Flue Cured Tobacco
Ind. Eng. Chem. 28, 160-169 (1936)

(6) Faitelowitz, A.
The Importance of the Acidity of Tobacco for its Hygienic Evaluation
Z. Untersuch Lebensm. 60, 518-523 (1930)

(7) Gabel, N. O. and G. I. Kiprianov
Reaction of Tobacco Smoke as an Index of the Quality of Tobacco
Ukrainskii Khim. Zhur. 5, Tech. pt. 107-84 (1930)

(8) Gaertner, K.
Evaluation of Tobacco on the Basis of Its Chemical Composition
Magyar Chem. Folyoirat 44, 19-30 (1939)
C.A. 33, 7485 (1939)

References

(9) Garner, W. W.
Relation of Nicotine to Quality of Tobacco
U. S. Department of Agriculture, Bureau of Plant Industry,
Bulletin 141, 5-16 (1909)

(10) Garner, W. W., C. W. Bacon and C. L. Foubert
Research Studies on the Curing of Leaf Tobacco
U. S. Department of Agriculture,
Bulletin 79, 40 pages (1914)

(11) Garner, W. W., C. W. Bacon and J. D. Bowling Jr.
Cigarette and Cigar Tobaccos
Ind. Eng. Chem. 46, 970-974 (1954)

Garner, W. W., C. W. Bacon, J. D. Bowling and D. E. Brown
The Nitrogen Nutrition of Tobacco
U. S. Department of Agriculture,
Technical Bulletin 414, 77 pages (1934)

(12) Gawrilow, N. J. and A. W. Koperina
Investigations in the Field of Tobacco Chemistry IV,
Method of Analyses for Tobacco Smoke
Biochem. Z. 251, 25-32 (1931)

(13) Haley, D. E., F. D. Gardner and R. T. Whitney
Nicotiana Rustica as a Source of Nicotine for Insect Control
Penn. Agr. Experiment Station, Bulletin 188 (1924)

(14) Hall, N. F. B. and J. C. Earl
The Chemistry of Australian Grown Tobacco
J. Council Sci. Ind. Research 8, 277-90 (1935)

(15) Koenig, P.
Chemical and Physical Differences between Heavy and Light Tobaccos
Z. Untersuch Lebensm. 70, 26-35 (1935)

(16) Koperina, A. W.
Investigation in the Field of Tobacco Chemistry, Resins of Tobacco Smoke
Biochem. Z. 256, 154-44 (1932)

References

(17) Lehmann, K. B.
Chemical and Toxicological Studies on Tobacco, Tobacco Smoke and Tobacco Smoking
Arch. Hyg. 68, 321-420 (1909)

(18) Muller-Thurgau, H.
Starch and Sugar Behavior in Ripening and Drying Tobacco Leaves
Landw. Jahrb. 14, 495-512 (1885)

(19) New York Agricultural Experiment Station
48th Annual Report, pages 24-25 (1927)

(20) Pyriki, C.
Comparative Investigations on Resinous Components of Oriental Tobacco and Its Smoke
Z. Untersuch Lebensm. 80, 48-61 (1940)

(21) Rieser, A.
Chemical Composition and Quality of Turkish Tobacco
Inhisarlar Tutun Institutusu Raporlari 1, (1) 38-47 (1937)

Rieser, A.
Contribution on the Question of a Nicotine-free Turkish Tobacco
Inhisarlar Tutun Institutusu Raporlari 1, (2) 99-106 (1937)

(22) Shmuk, A. A.
Taste Quality of Tobacco as Related to Chemical Composition
Bull. Acad. Sci. U.S.S.R.
Serie Biol. 955-968 (1939)

(23) Symons, J. W.
Canadian v. American Flue Cured Tobacco
Canadian Chemistry and Metallurgy 19, 259-265 (1935)

(24) Wenusch, A.
The Appearance of Resins in Tobacco Smoke
Z. Untersuch Lebensm. 69, 81-85 (1935)