Substitutes for Natural Flavors

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A brief statement of varied food preferences and tastes against a background of world nutritional needs is given. Discussion of requirements for flavoring new foods (particularly the spun and textured soybean types) within the current U.S. legal limitations is presented. The currently approved group of flavoring ingredients must be extended to allow for the development of additional kinds of flavors, *e.g.*, meat and vegetables. Natural sources for flavoring materials are not unlimited in supply; therefore, the expanding food industry will become ever more dependent upon synthetic counterparts for naturally occurring substances. A suggestion is made for broadening the list of permitted materials to include all aromatics found in foods.

Science fiction writers of the early part of this century predicted that in the future man would be eating synthetic foods in the form of pills and fluids which would do away with the bulk foods currently enjoyed by the human species. Astronauts traveling to the moon are enjoying concentrated spreads and sandwiches presented in a form that is momentarily foreign to us earthlings. The day that man can convert leaves, grass, algae, and petroleum into food has arrived.

THE EVOLUTION OF TASTE

However, even though we are at the beginning of the Space Age, foods still tend to look and taste like the foods to which our ancestors were accustomed. They are available in new forms but are basically recognizable as food products. The day of the food pill is probably far off in the future and possibly will never happen. Calder (1967) has said, "The popular myth that the day will come when science will feed a man on a few little pills each day is without foundation. Energy has to be supplied to the human body in a mild chemical form, which immediately implies a volume at least approaching that of present day diets. Indeed, the aim of industrialized food production should be something as substantial and palatable as present meals in the prosperous countries." Morris (1967) states that mankind, in his evolution from a primitive species, has carried with him certain taste preferences which, in spite of our advanced civilization, still play an important subconscious role in his daily eating habits. He points out that primitive man learned to eat various vegetable products before he achieved his taste for meat. Man undoubtedly learned by an accident that fire improved the taste of this latter source of food, and thereby he was able to expand the range of flavor sensation available from his primitive sources of nutrition. Hence, the diet of Western man makes use of a vast variety of food products derived from the cereals, such as corn and wheat, from animals, such as beef and chicken, and even from insects, such as honey. Peoples in other parts of the world have further expanded this base to include rice, plantain, and locusts. Because of mankind's wide taste preferences, bland food products generally are not consumed with relish by the largest segment of the population, and we find that historically man has added either salt, sugar, and/or a considerable variety of spices and herbs to his daily fare so that he might enjoy the moment taken to replenish his source of energy. The enjoyment of food is perhaps as important to man's psyche as is the nutritional aspect to his body.

Thus we see that, depending on the area of the world with which one deals, it is generally found that the most popular food products are those which have a rich tasty flavor and are at the same time nutritious and rich in protein. Consider for the moment Viet Nam, where a population is dependent on rice. To make this food more attractive, the inhabitants use tuk trey, a fish sauce made by fermenting fish. This substance not only adds a very interesting flavor to the food, but also introduces a desirable allotment of protein. By our standards, the resulting mixture may seem rather unappetizing because the taste would be foreign, but then others may view the continental preference for Bleu cheese to be rather strange.

PROBLEM OF ACCEPTANCE

Because of mankind's preference for natural type foods, even though they may exist in new forms, the flavors associated with such foods must be available for the complete satisfactory sensation of taste. This is particularly in evidence with the spun and textured soybean protein meat-type substitutes. Such products are as nutritious in their base states as they would be in the finished state which is offered to the public. However, the manufacturers of these new foods have recognized that in order for these products to gain acceptance in the market place, the finished food will have to resemble

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other foods with which the public is already familiar. The FAO Congress held in Rome (1965) put the point quite firmly: "The most critical and difficult aspect in introducing these products for large scale use in the human diet is acceptability and marketing." Of the two factors, we believe acceptability or palatability is far and away the more important. The substitute meat-like material will have to look like, feel like, and, most importantly, taste like its natural counterpart. This latter consideration has presented a tremendous challenge to the flavor industry. Today, its chemists are diligently working to prepare the needed flavor specialties.

Twenty years ago there was no crying need for beef, chicken, lamb, or pork flavors; in fact, the flavor chemist was only called upon to prepare mixtures of spices and herbs which would complement the meat product. Today, the demand exists for the flavor of the meat itself. The same is true for other basic commodities. Flavors simulating potato, tomato, and corn have been fabricated to supplement and complement new foods or to replace them with a substitute product.

WORLD NEED

Nutritionists have advised that, because of the rapid growth in population, vast areas of the world will be suffering starvation by the year 2000. Best estimates indicate that there will be at least twice as many people on Earth then as there are today. Areas already overpopulated will become more so. In many areas food shortages already exist. To meet their barest needs, production of vegetable foods will have to double. This need is hardly uniform, as is quite obvious, for tremendous disparities exist. According to Slater (1965), the requirements for food production in Asia will, in this time, have increased fourfold. There will be a demand for $2^1/_2$ times as much output in Africa and a need for a threefold increase in the Near East and Latin America. Scientists worldwide are working today to counter this problem, and this work possibly will offer a remedy before the crisis arrives. Yet any solution which is recommended must take into account mankind's background and the psychology of food. It will not be enough for the food to be merely nutritionally correct; equally important, it must prove to be acceptable when measured by the various criteria of man's taste. Here we speak of taste in the aesthetic sense as well as in the sensory realm. Henahan (1966) has stated the case rather succinctly " . . . the problem is compounded by the fact that even when a man is starving and knows the reasons for it, he is still particular about what he eats. A man may agree that a protein concentrate from fish, soybean, or some other source will do him good, but he is still at the mercy of culinary traditions that stretch back to the beginnings of his civilization. If he has a choice between a handful of rice and a (more abundant supply of a) suspicious looking powder, he will probably choose the rice and hope it gets him through another day. Even though it is now possible to fabricate protein concentrates that look and taste like meat and fish, nutritionists continually struggle with the ingrained reluctance to try something new." We have seen where synthetic rice was prepared for the Indonesian people (New York Times, 1969) which was not acceptable because it did not appear or taste like the rice to which they were accustomed. Newspapers in Saigon reported that people were husbanding their meager savings to be able to buy native rice which, in their opinion, had a finer flavor than the imported rice, even though this imported variety was considerably less expensive. In India we have seen the effect of an attempt to feed the starving with wheat. This proved unfruitful because they had no previous history of eating wheat and they were reluctant to cultivate a taste for this foodstuff in spite of the basic food shortages to which they are constantly exposed.

DEVELOPMENTAL DIFFICULTY

With this background, we approach the synthetic foods of the future with a knowledge that such food products must be both appealing visually and organoleptically. Herein lies the paradox. Natural foods such as meat and milk will probably be unavailable for the masses when the year 2000 arrives. It will not be feasible to provide nutrition in this manner, for it will be uneconomical to depend upon a beast to convert plant carbohydrates into animal protein. However, the taste for these natural foods will still be there. Flavor chemists must somehow provide this. One will not be able to draw upon natural sources for flavoring materials and the chemist must create synthetic flavors duplicating natural flavors from whatever sources would yield such flavors in an abundant supply. For example, it has been shown at the present time that if all the strawberry flavor currently consumed in the U.S. were dependent on natural sources grown in the U.S., there would only be sufficient strawberry flavor to supply New Jersey for 1 year. Therefore, synthetic strawberry flavors at the present time are replacing much of the demand for this flavor sensation, the greatest percentage of which cannot be provided by natural sources.

Strawberry flavors have long been known to flavor chemists. In the earlier part of this century, their composition was rather crude, since they depended wholly on the use of low boiling esters and aromatic aldehydes for their characters. Clarke's (1922) employment of high concentration of amyl acetate and benzyl acetate is typical of early strawberry flavors. As additional new interesting chemicals became available, we notice a steady movement away from the highly volatile and ethereal style of flavor, and what was once only an approximation of the taste of the fruit later became an attempt to match nature more closely. Of all the new aromatics added to the chemists' arsenal, none was more important than so-called aldehyde C-16, or more properly, ethylmethylphenyl glycidate. As an interesting sidelight, this compound has not as yet been discovered in nature. But analogously, aldehyde C-14 or γ undecalactone, which is used in peach flavors, has never been found in nature. It had been used for years in peach flavors when analysis (Jennings and Sevenants, 1964) finally showed the presence of γ decalactone in peach juice. The difference between the molecules is only one carbon atom. Flavor chemists were almost correct in their employment of γ undecalactone. They used a substance, not knowing of its presence in nature, yet were basically correct as to structure and missed achieving complete identity by only one carbon atom. Aldehyde C-16 has a remarkable strawberry-like character and someday it or at least a close homologue of it may too be found in nature. Judicious use of this material made more satisfactory simulations possible. Work has continued and has been considerably amplified in the search for a better understanding of strawberry flavor, as evidenced by the classic investigation of the Western Regional Research Laboratory (McFadden *et al.*, 1965) which reported 150 different components. Many of these were shown to be present by other investigators. However, the discovery of certain hexenyl derivatives was of true significance. Synthetic strawberry flavors today contain most of the ingredients found in nature in their proper relationship, and therefore they taste more

natural. Yet since they are man-made, they can be so constructed as to withstand the rigors of food processing to which these might be exposed. High temperature application such as that encountered in the manufacture of hard candies requires certain modifications to withstand processing. The flavor strength of the juice even in its most concentrated form is insufficient to allow for the production of such a confection, and attempts to use the true fruit flavor for this purpose results in a sticky mass that has been caramelized beyond recognition. The high levels of this type flavor which are required would unbalance the formulation of the candy, and its high acid/sugar ratio would be altered in the high temperature which is encountered. Utilizing an artificial flavor, the candy maker's formula is not further complicated by the introduction of unwanted fruit sugar and acid. The flavor manufacturer, while maintaining fidelity of characteristics, has included fixatives in the complex to reduce the volatility of the total entity, thereby improving on nature.

PUBLIC UNDERSTANDING

The attitude of the food industry toward synthetic flavors has been a stigma for many years. The term "artificial flavoring," which is required labeling for food products containing imitation flavors, sometimes raises an objection by the consumer before he even tastes the food product. In the general public's view, imitation, synthetic, or artificial are often synonymous with lower quality. This is particularly true for food products, but is not the case in other fields such as tires or clothing. In these cases the average person accepts nylon as superior to a natural fiber and synthetic rubber as superior to natural rubber. Why? Because he has been conditioned, through advertising, by these manufacturers to believe and accept the superiority of the synthetic product. Also, these synthetics do, in fact, offer advantages in price and durability which cannot be provided by natural sources.

Manufacturers of such products capitalize on the fact that their product is a new entity and not a synthetic. Most of us have seen the advertisements for Dynel which state that, "It is not fake anything, it's Dynel." Nylon originally competed with silk, but no one compares the two today. Nylon stands on its own merits. It is hoped that this situation will some day apply to flavors as well. Too long the food industry has been hampered by this situation. It is hoped that the public can be educated to accept synthetic flavors as an entity superior to natural sources. Perhaps the food industry will embark on such a course in time.

Such a breakthrough may be in the offing. Considerable interest has been spurred by the arrival of the soy protein foods, to which we have previously referred. Since Boyer patented the process for precipitating and spinning protein fibers back in the early 1950's, certain of these foods have been introduced to the market, although in a limited way, appealing to special religious and dietary groups. The outlet represents but a portion of the total opportunity, for the finished fibers present a raw material that can be treated in many imaginative ways to develop new and unusual foods. Some are already looking into the future and we observe that "bits and chips" of ideas are reaching the supermarket shelves. But if these new foods are to be categorized as "imitation this" or "synthetic that," they will find difficulty in gaining acceptance; however, were they to be dependent on natural ingredients for flavor, they could not even exist.

Today's buying public is a highly sophisticated one, and its standard of taste has likewise been broadened considerably beyond the ethyl acetate, amyl acetate level. These aromatics are still very useful, but they cannot help to bridge the gap of our current flavor development needs. The industry is now becoming much more involved in the "reaction product flavors" mentioned by Kiratsous (1969). Many of these condensation products have a fundamental meat-like aroma that could prove useful in the expansion of the available flavor spectrum. Further work is being pursued to utilize and understand the flavor precursors naturally present in food in order that we might attain fuller value from existent sources. We note that supplementary flavoring materials, monosodium glutamate, the nucleotides and hydrolyzates from various materials, are receiving ever greater prominence in new product development efforts. Flavor chemists are using an increasing array of ingredients. Because of this, modern flavors are tending to reproduce natural flavors and often improve on them.

Nature may not always be right when it comes to making a flavor. Witness the variation in crop years. Quality vintage wines occur only every few years, except in California. Foods which are transported over long distances often reach the consumer when the flavor has passed its peak. When synthetic foods are produced, these will be balanced nutritiously to eliminate the variations which nature produces and standardized with constant peak flavor character which will eliminate the flavor differences associated with nature. This is not an attempt to raise substandard qualities, but to provide more uniform enjoyment of food. The standardized flavor will be the best possible flavor, duplicating the finest flavor from nature. We will no longer be dependent on the amount of sunshine which the grapes or oranges receive. Food need not be picked at the peak of perfection and then attempts made to preserve this flavor. A flavor chemist will theoretically be able to reproduce the flavor of a food product, such as vine ripened grapes, and this flavor can be reproduced at will in any product, at any time, under any conditions.

HOPE IN THE UNKNOWN

How will this be achieved? Certainly not by using the historical approach. We are at the beginning of a revolution in flavor technology in which the subjective character of organoleptic evaluation is gradually being eliminated. For flavors to be reproduced consistently, the degree of error which is implied in any subjective evaluation must be eliminated or reduced. Organoleptic evaluation should be supplemented with an objective evaluation which can be provided by gas liquid chromatography and other instrumental techniques. However, one must not lose sight of one basic concept—that flavors made by humans are offered for human consumption. Flavors made exclusively by machines will be acceptable only to other machines. Therefore, the flavor chemist who prepares flavors using information provided by instruments must temper this information with his own creative sense to achieve the best possible flavor. I am certain that many flavor chemists have had the unrewarding and frustrating experience of reconstructing a flavor from the voluminous information made available by instruments and found the resulting product quite different from that which was expected. The chemist must behave more or less like the French chef who adds a soupsçon of this and a pinch of that to create the pleasant aesthetic effect so different from one less skilled in culinary arts.

For the flavor chemist to have available such materials, the organic chemist plays an important role. Once the analysis of a food product reveals the presence of a new substance, it should be possible to create this synthetically and

thereby eliminate the flavor industry's dependence on nature for this particular substance. Such has been the situation with some flavoring materials, and most recent production figures (U.S. Tariff Commission Reports, 1966) indicate that over 1,300,000 pounds of cinnamic aldehyde were synthesized to meet recent requirements. We do not mean to imply that this is a complete replacement for cinnamon, yet it is fundamentally important for the basic characteristic of this natural flavoring material and serves as the main building block for substitutes. The breaking of the secret of chamomile or ginger oils may still result in the need for aromatics that cannot be synthesized economically, and we will remain dependent on nature for certain unusual nuances. What is obvious, though, is that a great deal of research is currently being done in this area and that much more will have to be done. Hopefully, while determining the actual presence of currently unknown compounds in nature, homologues as useful as ethyl vanillin and ethyl maltol will be developed.

LEGAL COMPLICATIONS

As problematic as the scientific aspects are, other restrictions exist of a legal nature. What is the legal status of a synthetic material, which is an actual counterpart of a naturally occurring substance when used in a food product? Present government restrictions prevent its use until it is cleared via a tedious, costly petition route to the Food and Drug Administration. Does it really make any difference if 4-(2,5,6,6-tetramethyl-2-cyclohexen-1-yl)-3-buten-2-one (irone) occurs in nature or is produced synthetically? The flavor effect is the same if it is used correctly. We should not be faced with the restriction that a synthetically reproduced natural component would be prohibited unless cleared by the red tape entailed. Until a recent ruling by the Food and Drug Administration, synthetic ethyl alcohol could not be considered for employment in food products. Prior to a modification in the Compliance Policy Guidance Systems, only alcohol produced from fermented foodstuffs could be used for such purposes. However, recognition of the need to directly utilize grain and fruit for food, rather than as a medium for fermentation, has finally brought about a change in thinking. If we are seriously concerned about possible world food shortages, revisions in current practices and philosophies will have to be effected. And although the government has been willing to alter the policy for kinds of ethyl alcohol to be used in food, its labeling demands to indicate the source of such alcohol are sure to hamper the adoption and wide use of the synthetic kind.

Another cloud on the horizon may be that the authorities will take the position that any material reported in nature can be used to build a flavor, providing that use of this newly discovered ingredient be included in foods at a concentration not to exceed that found in the original source. Here again, the flavor chemist will still be strongly restricted. Looking to our experience with vanillin, were we to be hampered by being required to limit the employment of this useful aromatic to the amount known to be present in pure vanilla extract, many widely consumed and enjoyed vanilla flavored food products would not be available. First, we should recognize that the total world supply of the natural commodity would be completely inadequate to handle the demand. Second, we must also recognize that the flavor industry considers 1 ounce of vanillin to be the flavor equivalent of 1 gallon of vanilla extract. Yet, this latter may be said to contain roughly 10 g of vanillin. Here we have about a threefold margin, and with this ratio, vanillin is very useful and important. Were its usage limited to the amount present, the many imitation vanilla flavored products currently using this as a prime ingredient would not exist today.

THE SOLUTION TO FLAVOR NEEDS

Our feelings are that if the food for tomorrow program is to advance today, there will have to be a definite broadening of permitted materials. To illustrate our point, certain furanones have been reported among the volatiles of beef flavor by Tonsbeek and coworkers (1968), and after investigation have been assumed to be responsible for the meaty aroma of one of the fractions isolated by Hornstein and Crowe (1964) during their basic work on the determination of meat flavor. The dihydrofuranones were also mentioned by Chang *et al.* (1968) as being in the flavor of boiled beef, and we encounter them again while viewing the results of the analysis of the volatiles of roasted cocoa beans and roasted coffee. Considering a description of their characteristics, 4-hydroxy-2,5-methyl-3-(2H) furanone being caramel-like while 4-hydroxy-5-methyl-3-(2H)-furanone resembles roasted chicory, one can anticipate the discovery of their presence in other natural food flavors as the light of investigation is focused to illuminate more obscure corners of our knowledge. Yet, by our present law, these useful and essential components must be disregarded, for the flavor industry was not aware of them prior to 1958 and therefore was not employing them in formulations as such. The same case can be made for the pyrazines, and with even more telling effect. At present the FDA has not made provision for their inclusion in flavor, although many in our industry judge them to be safe. Yet as we delve deeper into the nature of the aromatics responsible for this quality in food, compounds of this class appear with greater frequency. The permitted aromatics are generally oxygenated with few sulfur or nitrogen containing substances. It is in the latter categories that the greatest discovery of new flavor materials is possible.

Many basic investigators such as Bondarovich *et al.* (1967), Gianturco *et al.* (1966), Stoffelsma *et al.* (1968), and a number of others have noted the importance of the pyrazines in the flavor of some foods—coffee, cocoa, and peanut—and have suggested that such complexes could be considered responsible for the flavor of other roasted and cooked foods. We are quite certain that this is correct when one views the characteristic flavor of pyrazine or some of its more widely reported homologues like 2,3-dimethyl or 2,5-dimethyl. All of these have peculiar nut-like aromas which could make them most useful in new product development efforts, and with their rather significant potency, small quantities would be sufficient to achieve singular results. However, at this moment we must refrain from including them in our work, regardless of how useful they could be, or how widely they are distributed in nature, and how small an amount would be needed for the particular end. Yet to attempt to develop some food flavors without ingredients in this class will be foolhardy, for the natural effect the consumer demands requires the inclusion of the synthetic counterparts of naturally occurring constituents. As we have previously stated, it will not be possible to juggle the list of currently permitted aromatics in any way to produce a mixture resembling many of the naturally occurring constituents. To eliminate the thiols and other sulfur containing compounds, the furans and even some newly found lactones, from consideration will hamper the development of the needed new food products. If we are to attack the world hunger problem with hopes of success, we should not be restricted by the previous limits of our analytical tools, but rather we should be employing the fruits of our discovery and new

knowledge to advantage. If we are to convert fish into bread, and soy into meat, we will need all of our ingenuity and every tool, for only then do we stand a chance of combatting the protein problem. Technology and common sense must move forward together.

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Received for review October 20, 1969. Accepted July 31, 1970. Presented in symposium on Synthetics and Substitutes for the Food Industry, Division of Agricultural and Food Chemistry, 158th ACS Meeting, New York, Sept. 1969.