Synthetic Flavors for Fatty Foods

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Flavorings for fatty foods have to be largely fat-soluble. Butter or cream flavor can be imitated by using lower fatty acids, carbonyls, alcohols, esters, lactones, or aromatic compounds. Other ingredients of fatty foods may interact with added flavor components. Natural flavors of, *e.g.*, virgin oils, oil nuts and seeds, and fresh oil fruits have been investigated extensively. Also flavors of roasted products can be imitated, although less sophisticatedly. In several flavoring problems, local demands may play a predominant role. In the near future, combinations of now available synthetic flavors with fatty foods will yield new products.

The definition of fatty foods is rather arbitrary. It may give an indication of the percentage of fat with respect to the total weight or the percentage of fat with respect to the water-free mixture (dry matter). In Table I a number of important foodstuffs and the percentage of fat they contain with respect to the total weight are listed. It seems, however, reasonable not to make a strict distinction in classification and, for instance, to consider also various types of cheese—even if they contain a large amount of water—as fatty food.

It might even be better to make a classification according to the amount of calories in the fat components. Table II shows such a classification for the principal fatty foods in the average diet of some countries (Stroink, 1967). The values relate to examples from developed countries, but in other countries such as India, ghee (buffalo butter) and its vegetable substitute, vanaspati, may appreciably contribute to the fat intake. In general, however, the caloric intake in these countries is mainly derived from carbohydrates, and fat plays a minor part.

When we consider the various triglycerides which form the main components in natural fatty foods—in contrast to the fatty acids produced by the petrochemical industry—we find an enormous diversity in composition and, consequently, in melting behavior. Mixtures of these triglycerides are liquids in one product and semiliquids in another, while also very rapidly melting products, such as cocoa butter, and hard products, such as bakery fats and tallow, can be obtained. The melting behavior can be influenced considerably by a change in the crystal mix as a result of interesterification, and by the type of emulsion used.

The type of fat, the melting behavior, the type of emulsion, as well as food additives may also have a marked influence on the taste perception (Polak, 1968).

FLAVOR INVESTIGATIONS

The first flavor investigations started on dairy products, particularly butter. As early as 1899, a patent was granted for the application of butyric acid in margarine (Poppe, 1899), and in 1929 diacetyl was found to be an equally important factor in butter flavor (Van Niel *et al.*, 1929). The amount of diacetyl is different for each type of butter and varies from 1 to 4 mg per kg. It is formed from citric acid present in milk (0.1%) by the lactic acid fermentation process commonly applied in butter and margarine factories. This lactic acid fermentation is a carefully controlled process in which *Streptococcus lactis* and *Streptococcus cremoris* form D-lactic acid from lactose and the so-called flavor organisms *Streptococcus diacetylactis* and *Leuconostoc citrovorum* form C_4 compounds (*e.g.*, diacetyl) from citric acid. According to De Man (1956), α-acetolactic acid is the intermediate compound, which is converted into diacetyl by oxidative decarboxylation. By aerating the fermenting milk, up to 100 mg acetyl per kg of milk may be formed; without aeration only 2–5 mg is formed.

The production of diacetyl by the fermentation process has now partly been replaced by a chemical method: oxidation of ethyl methyl ketone. Diacetyl is added to margarine in a concentration of a few mg per kg.

The flavor substances formed during lactic acid fermentation of milk or skimmed milk had never been clearly analyzed until about a decade ago, when it was found that certain naturally occurring substances, even in extremely low quantities, contribute to the flavor of butter. At the moment we also know that a number of volatile substances formed from specific fatty acids in butter by hydrolysis, autoxidation, or decomposition contribute to the butter flavor. These volatiles were analyzed in many research institutes.

The methodology of the research into flavors has been discussed in detail at various symposiums and seminars. An idea of the way in which this research was performed 15 years ago in our laboratory is given in Figure 1.

This work has always been and, in fact, still is based on organoleptic perception, as is shown in Figure 2, where some streamlining has been introduced. Adaptation to a specific problem is, however, always necessary.

The principal butter flavor components, on which excellent reviews have been written (Kinsella, 1969; Chandan *et al.*, 1969; Schultz *et al.*, 1967; Boldingh, 1969; Boldingh and Taylor, 1962) are:

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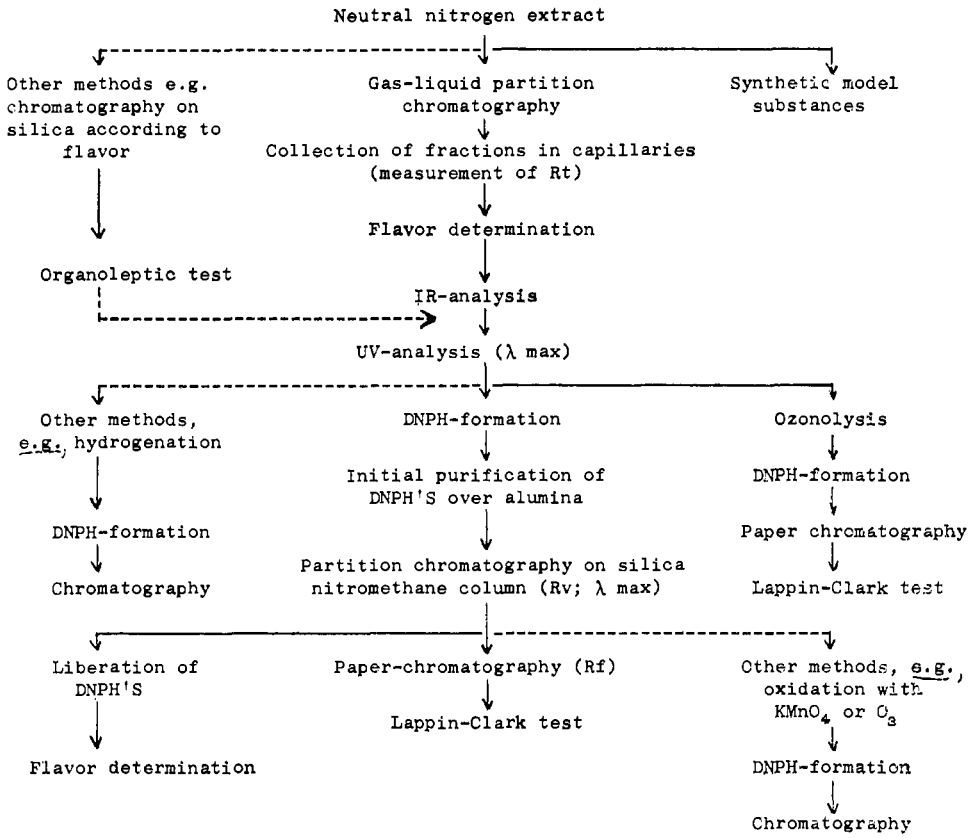

Figure 1. Scheme for the analysis of the degassing products

Aldehydes

C_1–C_{12} aldehydes
2-methylpropanal
2-methylbutanal
phenylacetaldehyde
4 *cis*-heptenal
2-hexenal
2-octenal

Ketones

C_3–C_{15} ketones
3-heptanone
diacetyl
acetoin
phenylpropanedione

Alcohols

C_1–C_{10} alcohols

Lactones

C_8–C_{16} γ-lactones
C_6–C_{18} δ-lactones
γ-lactone of 6-dodecenoic acid
δ-lactone of 9-dodecenoic acid
bovolide

Fatty acids

Straight chain C_2–C_{12} fatty acids with even number of C-atoms

Esters

C_1, C_2, C_{10} methyl esters
C_1, C_2, C_4, C_6–C_8, C_{10}, C_{12} ethyl esters
Methyl benzoate

In mixtures of emulsions of fat and water, most of these butter flavor components, even substances as volatile and polar as diacetyl, have a partition coefficient directed to the hydrophobic phase. During production of the margarine emulsion, when the oil phase is still completely liquid, the greater part of the flavor remains dissolved in this phase. Also towards the end of the processing, when crystallization takes place, the flavor stays dissolved mainly in the residual oil phase. Some of the oil droplets are subsequently occluded in the solid phase, trapping the flavor.

The taste of a very fresh margarine is unbalanced. The aroma is based on a completely stabilized fat phase, so that flavor release is too rapid in a product which is too soft. The aroma is then perceived incorrectly. On the other hand, if the melting time in the mouth is too long, the flavor substances may be perceived in a wrong order, and sometimes too slowly, thus distorting and spoiling the flavorist's painstaking work. The next difficulty is that, on standing, other volatiles may develop: lower—melting fatty acids of the fat phase may be liberated by hydrolysis. Moreover, autoxidation may lead to the formation of undesired aldehydes with a strong flavor potency. They are formed during storage from the ever-increasing amount of hydroperoxides. These hydroperoxides differ from those formed from butter-fatty acids. The autoxidation products of butter therefore yield different off-flavors than the unsaturated fatty acids in the margarine, which originate from the normal natural fatty acids and from the unsaturated *iso*-fatty acids formed by hydrogenation. On the other hand, in most countries no

Table I. Fat Content of Some Important Foods

Product	Fat (%)	Product	Fat (%)
Salad oils	99	Low cal. spread	50–30
Frying oils	99	Salad dressings	60–20
Frying fats	99	Chocolate	32
Shortenings	99	Sauces	50–20
Ghee	99–95	Cheese	60–20
Vanaspati	99	Beef (mean)	13
Butter	84–82	Mutton (mean)	20
Margarine	84–82	Pork (mean)	22
Bacon	80	Poultry	4
Nuts	50	Fish (raw)	6.5
Mayonnaise	80–50	Hen eggs	11
Cream	50–20	Breadgrain	2
Milk	5–3		

Table II. Caloric Intake (per person per day) From Fatty Foods

Cal. value of	USA	U.K.	Germany	France	Italy
Fat in dairy products	268	357	321	312	133
Margarine, Edible fats and oils	427	368	451	314	343
Margarine, Shortenings	303[a]	186	231	72	13
Fat in meat, poultry, fish	438	408	341	313	110
Fat in miscellaneous	132	118	94	112	197
Total fat	1265	1251	1207	1051	783
Total diet	3100	3250	2960	2920	2740

[a] Edible oil included.

antioxidants are allowed in butter. As a result, butter deteriorates more rapidly on storage than a good margarine. However, although the off-flavors of old butter interfere with the flavor in the fresh product, the old product will nevertheless be assessed as butter. If the taste of older margarines should change as a result of the causes mentioned, it will easily be assessed as less satisfactory.

This phenomenon is illustrated in the differences in threshold value of the flavor of some aldehydes (Figure 3). These values were collected from literature data by Kinsella (1969).

Butter flavor is in fact very difficult to define, as different types of butter, such as sweet-cream butter, sour-cream butter, saltless, and salty butters are involved. Moreover, in some countries the butter has a very pronounced cheese taste, and in certain Mediterranean countries butters with the taste of sheep cheese are highly appreciated.

When developing different types of butter flavors, using the flavor components available, addition of various types of milk, skim milk—chemically or bacteriologically soured—whey, whey powder, or lactose specifically influence the eventual taste. Similarly, preservatives such as sorbates and benzoates have a specific taste which, in many cases, is dependent on the origin. The consumers in a country may easily get accustomed to such a specific taste. It is therefore understandable that addition of a flavor mix as marketed—added straight from the bottle of concentrate—will not necessarily lead to good results, because all the above-mentioned influences may interfere (De Jong, 1969).

A good example of the influence of salt in butter and margarine on the results of panel tests has been given by Albin *et al.* (1969). A large majority of the panel members appeared to be so accustomed to salt that a comparison between low-salt butter and margarine revealed much slighter differences with respect to product appreciation than the salted products. The reverse is found in continental Europe, where people are not accustomed to salted butter and margarine. A distinction is therefore difficult to make.

In many countries a certain group of consumers prefers a product that slightly deviates from the ordinary product, so that a certain diversification should be considered. In the near future an increasing number of fatty foods showing some relationship with the conventional dairy products will be marketed. In this connection the health aspect is a very important factor. A high content of polyunsaturated fatty acids, believed to counteract atherosclerosis, necessitates, however, a completely different flavoring because the low melting point and the different melting behavior of these

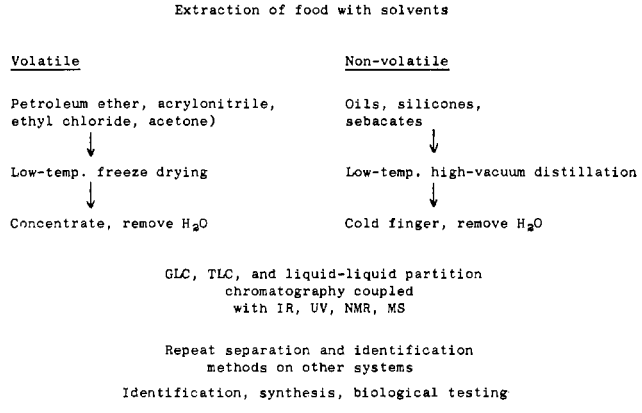

Figure 2. Isolation and analysis of flavor components

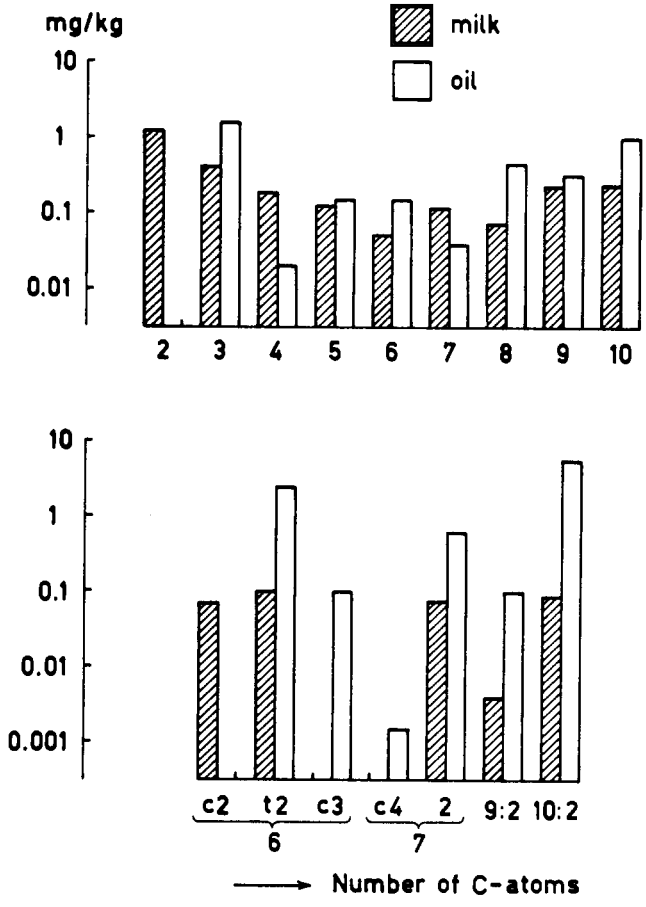

Figure 3. Flavor threshold values of *n*-aldehydes

fatty acid glycerides greatly influence the flavor impression. Kitchen use of hard or soft products will also be different and flavor release will strongly deviate. The off-flavors may form a not unimportant obstacle to heating of products which contain high amounts of polyunsaturated fatty acids.

VEGETABLE OILS

The flavor substances of oils, seeds, and oily foods, in particular coconut oil (Allen, 1965), sesame oil (Yamanishi *et al.*, 1967), sunflower and linseed oil (Lea and Hobson, 1965), roasted products, peanuts (Mason *et al.*, 1966), barley (Wang *et al.*, 1968), and corn (Reynolds Tobacco Co., 1968) have also been the subject of investigation, as have been virgin olive oil, which is of great importance for southern European and Mediterranean countries, and fresh palm fruit, which is much used in Africa to prepare meals. All these more or less natural flavors will certainly be imitated in the near future, so that new flavors can be applied to similar substrates or used in sauces, low-calorie spreads, or processed cheese. Research with respect to oils specific to tropical countries is still in an early stage.

Some oils, such as corn, olive, and groundnut, may contain flavors which will probably also be appreciated outside the countries of origin. Reversely, it will be tried to add flavors not specifically related to these oils and fats to see whether consumers will accept these types of food aroma.

So long as a flavor composition is satisfactorily fat-soluble, it is possible to make many new combinations for which a market may be found. Small children in Spain, for instance, like margarines with a fruity flavor, whereas their parents like butters and margarines with a very sharp cheese taste.

Many attempts have been made to combine spicy flavors with cheese, processed cheese, etc., and occasionally also with margarines, but the success is not too convincing. In the past few years, many flavors have become available, such as coffee, cocoa, roasted products, banana, pineapple (Schultz *et al.*, 1967), maple syrup (Filipic *et al.*, 1969), orchard fruits (Tang and Jennings, 1968; Sevenants and Jennings, 1966), citric fruits, different meat types (Losekoot *et al.*, 1969), lard like flavors, roasted and heated nuts flavors, and olive oil (Fedeli and Jacini, 1968). All these synthetic flavors can be used in products with a high fat content such as different types of dairy products and combinations of these; cream, artificial cream cheese—not only the ever used Cheddar type—spreads, toppings, health food, dressings, sauces, ready mixes, shortenings, salad oils, and bakery products.

DEFINITION OF NATURAL PRODUCTS

On the basis of what has been said before, one may wonder whether we can still speak of "natural" products. Can we indeed speak of "natural" in the case of butter when we consider that the milk was, in fact, meant for calves. This milk is subjected to various treatments such as souring, intensive churning, treatment with microorganisms, pasteurization, washing, and kneading, so that finally an oil/fat emulsion, called butter, is obtained.

Also, ghee prepared from buffalo milk and obtained by heating and evaporation in earthen pots over dung fires and stored sometimes for months in bags made of hides and buried in the ground is less "natural" than seeds and nuts or the oils obtained therefrom. A similar case is cheese. France produces at least 400 different types of cheese which are produced in different ways, where microorganisms not only play a part in the production but also during storage of the product.

If a synthetic cheese flavor is added to a spread, sauce, fat, or oil emulsion, the taste obtained is, in the majority of cases, only an approximation of the natural taste. Such products are often appreciated by people who like a different taste impression; moreover, the convenience and novelty aspect should not be overlooked.

It is expected that in the next few years a great many flavors will become available and, if FDA-cleared, will be applied. This will bring a greater variation in many products as regards taste and appearance. The preferences of the consumers, however, will have to be established before their wishes can be fulfilled.

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