The Reconstitution of Flavors[1]

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Abstract

The traditional purpose of flavor reconstitution in processed foods is to restore the depleted flavor level and quality. A more recent trend is the impartation of flavor to foods which have none, such as addition of synthetically reconstituted chicken flavor to soya protein and bacon flavor to hydrogenated fat. Flavor reconstitution of such foods can be approached from either a physicochemical study or by the use of organoleptic procedures. For best results a marriage of the two methods is required. The advent of modern gas chromatographic techniques has revolutionized the possibilities for the discovery of new flavor components and for determining the amounts in which they are present in food substances. While much time has been spent in the last 15 years gathering analytical data of this type, rapid progress can be expected in the future by the utilization of this information in areas of flavor reconstitution new to the flavor industry. The usual problems which arise when flavor reconstitution from analytical data is attempted are reviewed. The performance advantages and disadvantages of reconstituted flavors are compared against their natural counterparts.

Introduction

PRACTICALLY ALL OF THE PUBLISHED flavor research in various journals is concerned with the isolation and identification of volatile flavor constituents. It is rare to find any description of attempts to reconstitute flavor artificially with the volatiles that were identified. Often such attempts are very disappointing and we shall examine further as to why this is so. One can simply state that in general it is not possible to find out from the literature to what degree flavor reconstitution is feasible. Therefore, the flavor creator's task starts where published material leaves off. The recent interest in flavor reconstitution originates from the mutually reinforcing action of two developments. On one hand there are the greatly enhanced possibilities for carrying on flavor studies because of gas chromatography and allied instrumentation. On the other hand there is the new technology of convenience foods which has spurred the development of thousands of new consumer products.

As a result of the standardization of food processing, food manufacturers are very aware that flavor is one of the few ways in which they can differentiate their products from those of competitors.

The scope and technique of flavor reconstitution and some of the problems and pitfalls attendant to them are reviewed. The need for reconstitution may occur under various circumstances. For example, when a natural food is processed and lost flavor needs to be restored by addition of the original flavor recovered during processing. A successful example is the addition of recovered strawberry essence to cooked strawberry preserves (1). The flavor of strawberry is mostly of low volatility and these volatiles (2) can be recovered intact by condensing the water of the cooking operation and concentrating the aroma in it by fractional distillation. A less than successful example is the addition of recovered coffee aroma to instant coffee (3). The natural coffee aroma can be obtained from the condensation at low temperatures of coffee roast gases. The resulting liquid can be fractionated and selected fractions are added back into the instant coffee jar under a carbon dioxide atmosphere. When the housewife opens up the instant coffee jar for the first time, she gets the fresh coffee aroma which carries through into the cup of brewed coffee. Unfortunately, during the opening of the jar she lets in air. On standing the aroma is oxidized. After a few days we have instant coffee that is no better than if no aroma had been added. This is still an unsolved problem of reconstitution, due to the instability of the original flavor as well as that of synthetic duplication attempts.

Also needed is the reconstitution of aroma to a substituted food, such as margarine or artificial cream. Both are practically bland bases, ideally suited for flavoring. Why has it not been possible so far to find a flavor that is truly equal in performance to butter or cream? Flavoring problems of margarine illustrate so well many of the problems associated with flavor reconstitution. The answer to flavor reconstitution does not rest solely with identifying the aroma components and mixing them together. While many of the real important flavor constituents of butter are known (4) such as diacetyl, certain lactones, acids, aldehydes and ketones, not all of them are known. Flavor constituents that are known cannot always be used effectively because they need the yet unknown flavor ingredients to bring them out properly, they are not stable in margarine, we do not know the flavor precursors which seem to continuously generate unstable components in butter, and margarine and butter differ somewhat in physical behavior during melting and baking.

Three natural butter flavor components which are difficult to use as such in the flavoring of fats, are methyl mercaptan and *cis*-4-heptenal, both oxidized in margarine, although they seem to be more stable or continuously generated in butter, and the delta lactone flavor, which in margarine tends to disappear in storage, probably due to polymerization, and in butter it seems to last. In addition, on baking, butter releases new flavor ingredients characteristic of foods baked with butter, whether they be meat, fish or bakery products, whereas margarine does not yet give this baked butter effect at all. The flavor effect of butter on baking is possibly due to the release of flavor ingredients from precursors unknown to us and to the interaction of some of the butter constituents with the particular food.

Methods

There are two extreme approaches to flavor reconstitution. One is the strictly scientific approach, in which the natural flavor is qualitatively and quantitatively analyzed and reconstitution is made with the ingredients found. The other is strictly organoleptic: an experienced flavor compounder or flavorist, as he is often called, tastes and smells the food to be flavor duplicated and tries

Steps in scientific synthetic flavor reconstitution.

Isolation of flavor concentrate (1:100–1,000,000)
↓
Separation of components (up to 300, down to .01%)
↓
Identification ↓ Synthesis | Quant. VPC anal.
↓
Scientifically reconstituted formulation (correct until GLC identical)
↓
Organoleptically adjusted formulation
↓
Process and product development
- Application testing
- Physical formulation
- Synthetic process development

↓
Manufacture and end use in consumer product

FIG. 1.

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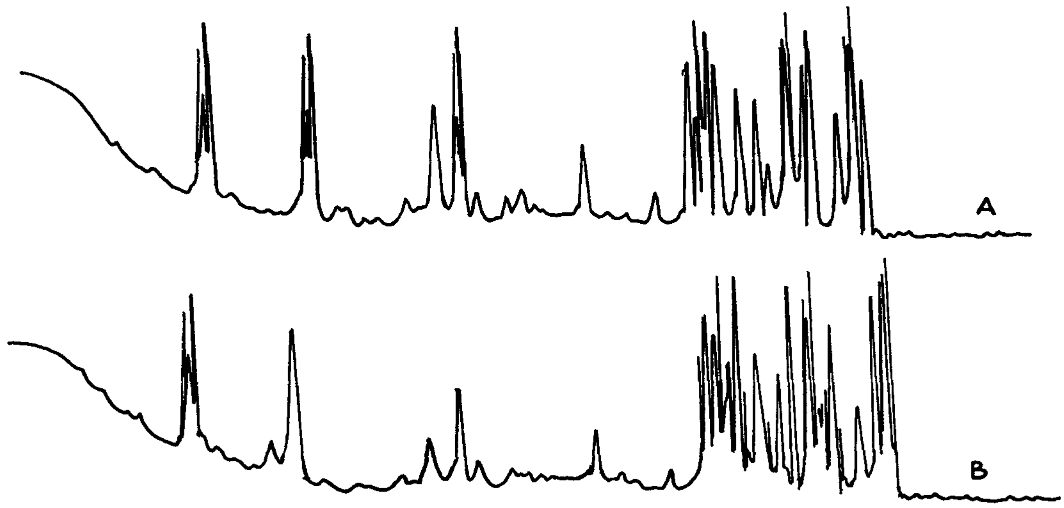

FIG. 2. Upper curve (A): Natural California lemon peel oil, lower curve (B): Synthetic lemon peel oil.

to create a similar flavor note by associating the flavor notes that he detects in the natural flavor with the flavor of aroma raw materials with which he is already well familiar. It should be noted that there is not necessarily an apparent structural connection between the chemicals he uses and the chemicals responsible for the flavor in the natural food. Either approach by itself is unlikely to be satisfactory. The combination of both is mostly likely to give optimum results.

Let me illustrate the limitations of the scientific approach (Fig. 1). The various steps likely to be followed start with concentrating the flavor, anywhere from 100 fold to a million fold. This is followed by the separation step of the various flavor components, usually numbering from a few dozen up to 300. The concentration in which these components are still traceable in the flavor concentrate may be as little as .01%. After or during the identification step those components that cannot be purchased from a commercial source will have to be synthesized. At the same time some quantitative GLC data will be necessary for a scientifically reconstituted flavor formulation. The first formulation usually has to be corrected with the help of GLC a number of times until one has a curve that closely resembles the one of the original concentrate. Finally, a few organoleptic adjustments may have to be made, usually to decrease flavor notes that stick out too much. At this stage a sample of the formulated flavor is in a bottle; however, a long period of process and product development is needed before a marketable flavor composition can be obtained.

There is a tendency to forget that the reconstituted flavor is unlikely to be much better in quality than the concentrated flavor isolate used for the analysis. More often than not the concentrate is already defective and no longer representative of the original food flavor. Flavor losses are usually unavoidable during the extraction and concentration steps. A number of flavor components disappear, the proportions of components change, and new artifacts are created due to such reactions as hydrolysis, oxidation, polymerization, pyrrolysis and *trans* esterification. As the flavor analysis proceeds, the original flavor notes tend to gradually vanish, as it were, into thin air.

Gas chromatography, which is likely to be the method of choice for both the separation and for checking the scientific reconstitution of the volatile flavor components, has its own limitations. On the whole, it is a remarkably undestructive tool. However, high boilers tend to be held back on gas chromatographic columns so that their existence may not be noticed. Also certain coatings may hold back even more volatile components. For instance, recently we found that phenylacetaldehyde, phenylethanol and benzyl alcohol would not elute from a Ucon 13 coated capillary column.

As a detection instrument, the nose is still superior (5) for the lowest threshold compounds. Even the best GLC detectors may not be sensitive enough to show up organoleptically important trace ingredients. Flavor mixtures may seem to be very close on gas chromatography and yet show vitally important differences in flavor quality.

Figure 2 shows the reproduction of a natural and a synthetic lemon peel oil GLC curve. All of the main peaks of lemon oil have been identified and published (6). Putting these ingredients together gives a reconstitution pattern on GLC which is identical as far as the main peaks are concerned, but flavor quality-wise the synthetic composition is unsatisfactory. The weight percentage in which the natural lemon oil volatiles occur is not necessarily equivalent to their flavor importance. Table I shows the strength relation (as determined by one person) between some weak flavor components, on the left, and some powerful flavor components on the right. The strongest flavor component in this table, nonadienal, has been given a unit strength of one. The figures for the other components indicate that they are that many times weaker. In a flavor composition using the threshold value proportions, each component will be equally important in intensity.

Minor and trace ingredients with low flavor thresholds, often 100 to 1000 times less than the main ingredients, can play a very important role. A good way of representing this effect on a GLC curve of a flavor is to take the peak areas of each component and divide them by their threshold values.

Occasional reports about reconstitution successes in the literature have a tendency to be over enthusiastic and

TABLE I

Strength Comparison of Low and High Threshold Components

Type	Compound	Relative strength threshold in ppm × 1000	Compound	Relative strength threshold in ppm × 1000
Hydrocarbon	Limonene	3100	2 Methyl-naphthalene	40
Alcohol	Tertiary Amyl alc.	7800	Octanol	20
Heterocycle	Furfuryl alc.	15600	Indol	80
Aldehyde	Vanillin	200	Nonadienal	1
Ketone	Benzophenone	1600	β-Ionone	20
Acid	Capric acid	800	Phenyl acetic acid	200
Ester	Ethyl levulinate	7800	Ethyl caproate	80

TABLE II

Imitation Blue Cheese Flavor: Arbitrary Flavor Quality Components

Additives	% BWT	Intensity range 0–10					
		Buttery	Fatty	Moldy	Fruity	Pungent	Dirty
Diacetyl	.3%	.5	..	..	..		..
Butanoic acid	5%	.4	..	..	..	3	1
Octanoic acid	25%	..	2	..	..	1	.5
2-Undecanone	5%	..	3	3	..	..	..
Indol	.01%	..	..	..	..	..	.5
Ethyl valerate	2%	.1	..	..	3	..	..
Solvent	Q.S. 100%	1	5	3	3	4	2

Steps in organoleptic synthetic flavor reconstitution	Example
Smell-taste analysis of food or flavor concentrate	Blue cheese
↓	↓
Resolution into subjective arbitrary quality components	Buttery fatty moldy
↓	↓
Assigning of rough intensity value to each quality component	1 Buttery 5 Fatty 3 Moldy
↓	↓
Association of quality components with known flavor materials	Diacetyl Methyl nonyl ketone Methyl amyl ketone
↓	↓
Formulation of reconstituted flavor	.3% Diacetyl 5% Methyl nonyl ketone 1% Methyl anyl ketone
↓	
Same steps as in scientific reconstitution	

Fig. 3.

somewhat uncritical. I don't know of any publication of recent years, where if you put together the results of the scientific analysis, you obtain a flavor that is really acceptable without further adjustments.

Rare is the occasion where the flavor effect can be satisfactorily duplicated by a few key ingredients. Usually the flavor is a complex impression, due to the interplay on the olfactory apparatus, of anywhere from one half dozen to hundreds of aroma components (Fig. 3).

This brings us to the limitations of the organoleptic method of flavor reconstitution. First we must recognize that it is a craft rather than a science. As an artistic type of craft the approach is subjective and intuitive. The creative flavor compounder works very much like a creative cook. Flavor reconstitution becomes a matter of flavor interpretation and strongly reflects the flavorist's personality, as well as his cultural likes and dislikes. This means that a rancid note may be objectionable in one country or in one particular food and very desirable in another country or in another food. As indicated earlier, before the advent of gas chromatography there was little access to knowing the composition of natural flavors. The flavor compounder had to rely only or mainly on his ability to detect and recognize by taste and by smell the components or notes that were present in the natural flavor to be duplicated. This works something as follows. The flavorist analyzes a flavor by first registering odor qualities which he perceives and then by assigning to each odor quality a rough intensity or quantitative value. He then tries to associate these quality components or quality parameters with known flavor materials. A composition is made and adjusted many times until the right components and proportions have been found.

Let us say that he has a request to give a blue cheese flavor to salad dressing without blue cheese. He takes a piece of blue cheese, sniffs at it, tastes it and may detect the following subjectively analyzed perfectly arbitrary overlapping odor quality components: Buttery, fatty, moldy, pungent and dirty. If we give the intensity of each odor quality component an arbitrary value of 0–10, we can imagine a rough quantitative representation of: 1 buttery, 5 fatty, 5 moldy, 4 pungent and 2 dirty. Sometimes this is called a flavor profile. For the flavor chemist's purpose such a profile is only useful if the quality components can be associated with specific flavor raw materials.

Table II shows the relation between the quality components and some blue cheese flavor ingredients. The important point is that a single flavor ingredient can make a contribution to either one or to several quality components.

TABLE III
Different Compositions Can Give the Same Flavor Note

Ingredient	%BW	Fatty (Intensity 0–10)	Moldy	Fruity
Ethyl isovalerate	2%	..	..	3
2-Undecanone	5%	5	3	..
Total		5	3	3
Dibutyl ketone	10%	..	3	3
Octyl alcohol	2%	5	..	..
Total		5	3	3
Ethyl valerate	2%	..	..	3
Methyl amyl ketone	5%	..	3	..
Octyl alcohol	2%	5	..	..
Total		5	3	3

To achieve a flavor effect the compounder may select any combination of flavor ingredients having single or multiple odor quality components, as long as the sum equals the totals or, if he is very fortunate, he may find a single synthetic that covers most of the odor quality range. This is illustrated by Table III by showing some variations possible in the moldy-fatty-fruity notes. Here we have three groups of flavor ingredients, each group having a somewhat different composition but giving very similar flavor.

One can now summarize some of the advantages and problems associated with synthetic flavor reconstitution. To take the problems and disadvantages first: (a) Often, but not always, the original natural flavor is better tasting than the synthetic version. (b) The natural flavor presents less of a labelling difficulty; where a given food has standards of identity, the synthetically reconstituted flavor may require a change of label. (c) The natural flavor, in its non-volatile portion, often has a reservoir of flavor precursors which generate fresh flavor volatiles on heating, as in frying of meat, or baking with butter; substitute foods using synthetically reconstituted flavors are usually devoid of such precursors.

Some of the advantages of synthetic flavor reconstitution are: (a) The economics are usually much more favorable; the same can be said for shelf life and heat resistance. (b) The high concentration and usual absence of water allows for special applications such as the use of encapsulated flavors in dehydrated and powdered foods. (c) There is unlimited availability because of independence on one particular crop.

It is possible to delete undesirable components from the synthetic product which must be tolerated in the natural mixture. These could be components that are toxic, unstable, unpleasant or otherwise unwanted.

There is much better control over product quality in the synthetic reconstitution because of control over the quality and the proportion of the ingredients. In the natural product the flavor is subject to variation due to growing, harvesting, processing and storage conditions.

What will the future bring? As more and more complete data becomes available on the actual flavor composition of natural foods, we can expect continuously incremental improvements in the corresponding synthetically reconstituted flavors.

From the point of view of the oil and fat chemist, we can look forward to entirely new developments, such as giving a sesame oil flavor to cottonseed oil, or pork chop flavor to hydrogenated fat, if that is desired.

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