SYNTHETIC MEAT FLAVORS*

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There is little doubt that from a technical standpoint the flavor industry has advanced more in the past two decades than in all previous history. Today, completely synthetic fruit flavors can be created that possess the odor and flavor of either fresh or cooked fruit. Creative flavor chemists have the capability and "tools" to duplicate the metallic canned character that is characteristic of many of our canned fruits. Thus, not only has the flavor chemist duplicated nature but he is also concerned with duplicating flavors that are a result of modern food technology. Combining the talents of the flavor chemist with modern food technologists is resulting in the duplication of many whole foods, especially those being used as raw materials by the food industry. Synthetic dry and wet cheeses, synthetic tomato powder are realities today. These total synthetics will improve in quality and others will be added to the list according to the dictates of world economic conditions.

Unfortunately, synthetic meat flavors have not yet attained the state of the art that exists for citrus and fruit flavors. This is not because this important area of research has been neglected but, rather because reaching a complete understanding of the complexity of the chemistry of the variety of types of meat and poultry flavors is one of the most difficult and challenging problems of modern flavor chemistry. The complete understanding of meat chemistry requires the combined efforts and talents of analytical chemists, organic synthetic chemists, creative flavor chemists and food technologists. I believe that there is little doubt that this area of research is now being emphasized by every progressive flavor company. The huge potential markets that await flavors that can be successfully applied to meat analogs are providing the impetus and justification for this research.

Table 1 shows U.S.D.A. 1980 market penetration projections for soy protein products in the meat area (1). It is apparent from these projections that the immediate market for the next 10 years is ground beef products. Notice that the total meat replaced is approximately 3 billion pounds which translates to 2 million head of cattle and calves and 4 million head of hogs or, 4% of the estimated 1980 production. The major impetus for partial meat replacements are lower retail prices and at least in the U.S., diets containing lower cholesterol and saturated fats. Table 2 illustrates the cost savings that can be realized when 20 and 40% of the meat in hamburgers is replaced with extruded soy protein. The calculations assume 1.00 dollar per pound for boneless chuck and 25

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* Presented at the 26th Annual Reciprocal Meat Conference of the American Meat Science Association, 1973.

TABLE 1. PROJECTED PROCESSED, PREPARED, AND CANNED MEAT ITEMS AND POUNDS OF MEAT REPLACED, USING THREE LEVELS OF HYDRATED SOY CONCENTRATE OR SPUN PROTEIN, 1980

Meat items	Total pounds of processed meat items	Soy protein substituted for meat		
		Low level	Medium level	High level
	- - - -	Million lbs.		- - - -
Processed or prepared				
Cooked beef	113	0	0	0
Cooked pork	184	0	0	0
Other cooked meats	36	0	0	0
Fresh finished sausage	623	104	162	208
Sausage to be dried	257	28	56	79
Franks, weiners	1,399	233	363	466
Bologna	712	138	188	237
Other smoked or cooked sausage	783	152	207	261
Loaf, head cheese, chili, jellied products	359	7	14	20
Hamburger, including ground beef	5,194	866	1,484	1,948
Bacon	1,878	9	13	19
Other sliced meats	924	99	179	245
Miscellaneous meat products	535	74	117	153
Frozen foods--dinners, meat pies, etc.	942	7	12	17
Canned meats				
Plain meats	1,019			
Italian dishes	433	12	17	22
Mexican dishes	352	14	19	23
Stews and hash	355	18	28	35
Soup	894	1/	1	1
All other with meat/or meat by-products				
20% or more meat	274	14	21	27
Less than 20% meat	514	11	17	22
Total	17,780	1,786	2,898	3,783
Percentage of meat replaced in total lbs processed meat items		10%	16%	21%

1/ Less than 500,000 pounds.

Marketing Research Report No. 947, U.S. Department of Agriculture, Economic Research Service. 1972.

TABLE 2.

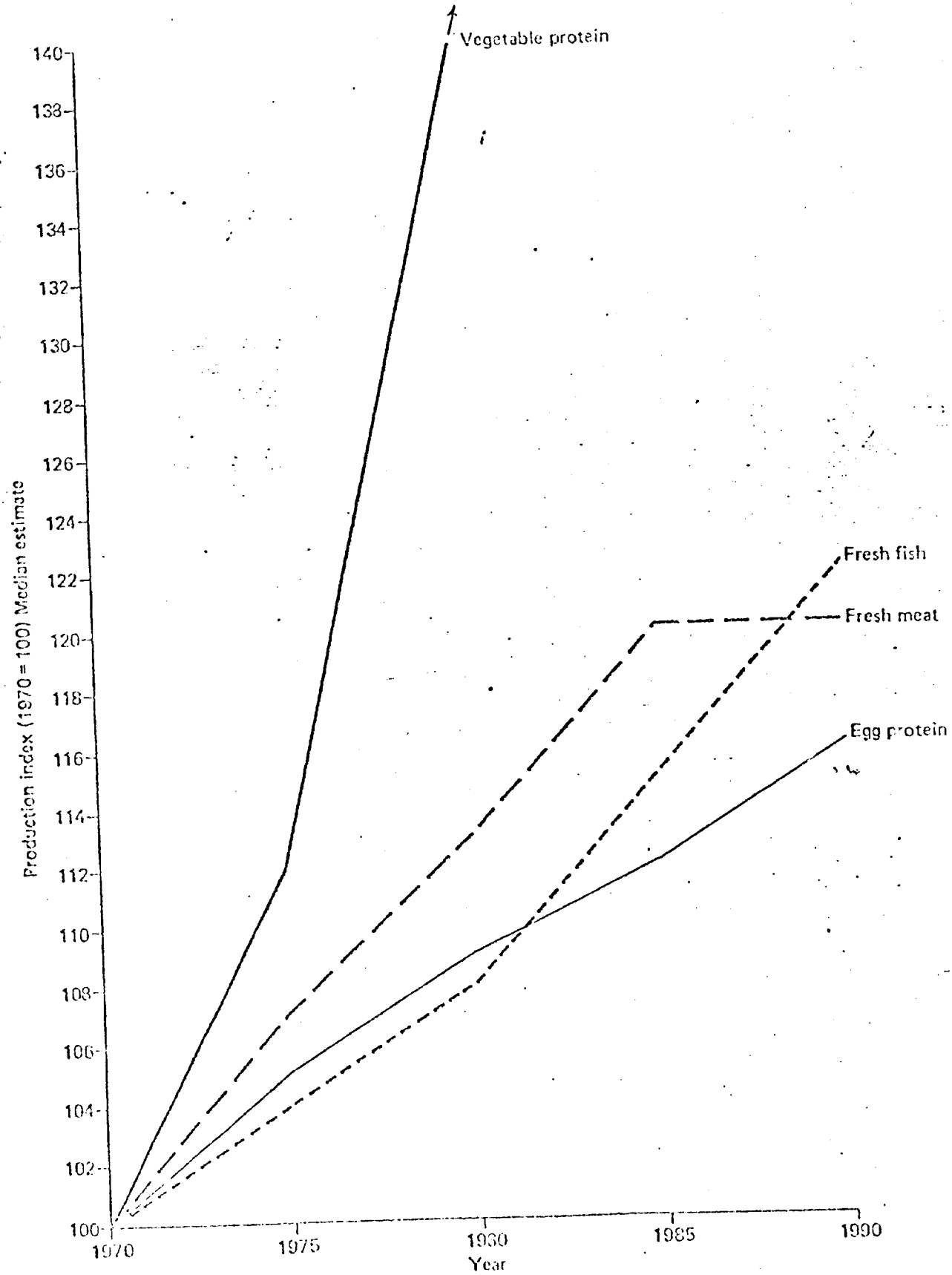
	Price/lb. (cents)	All beef		Patty plus soy concentrate		Patty plus extruded soy		Patty plus spun soy	
		% used	Cost	% used	Cost	% used	Cost	% used	Cost
Cost of beef-type patties--40% meat replacement									
Boneless chuck	100	93.33	93.3	53.33	53.33	53.33	53.33	53.33	53.33
Fat trim	5	6.67	.3	16.67	.83	16.67	.83	16.67	.83
Soy concentrate	25			7.50	1.88				
Extruded soy	32					10.00	3.20		
Spun soy (dry)	63							7.50	4.73
Water	0								
		100.00	93.6	100.00	56.0	100.00	57.4	100.00	58.9
Cost of beef-type patties--20% meat replacement									
Boneless chuck	100	93.33	93.3	73.33	73.33	73.33	73.33	73.33	73.33
Fat trim	5	6.67	.3	8.34	.42	8.34	.42	8.34	.42
Soy concentrate	25			3.75	.94				
Extruded soy	32					5.00	1.60		
Spun soy (dry)	63							3.75	2.36
Water	0							14.58	
		100.00	93.6	100.00	74.5	100.00	75.4	100.00	76.11

cents per pound for dry extruded soy. It is our opinion that the long term success and consumer acceptability of these products, especially at the 40 and 50% replacement levels, where extremely attractive retail prices are realized, is dependent upon the production of texturized protein that is bland in flavor, and the availability of synthetic meat flavors that function in these systems and impart a high quality, true meat flavor to the product.

The potential use of meat analogs is obviously not limited to the U.S. As an example, figure 1 taken from "Trends in the Food Industry Over the Next 20 Years" (2) illustrates the estimated production of major protein sources in the United Kingdom. Notice that by 1983 fresh meat production is projected to be level while vegetable protein production continues to increase rapidly.

The first synthetic meat flavors sold by the flavor industry were undoubtedly skillful spice blends that were and still are used in processed meats. Once the importance of monosodium glutamate and the 5' nucleotides became recognized and available, they were combined with spices to supply a portion of the brothiness of meat and to enhance the flavor of the natural meat. The introduction of high quality hydrolyzed vegetable proteins, which were then combined with the nucleotides and spice blends, resulted in the first meat flavors in certain areas of the food industry. For example, in the U.S., hydrolyzed vegetable protein products have almost completely eliminated the use of beef extract in dry soup, boullions, canned soups, and gravies. This replacement was brought about by economic conditions which resulted in increased costs of beef extract along with a consistent lowering in quality. There is no doubt that hydrolyzed vegetable protein based flavors are far from duplications of beef extract, but their gradual introduction and consumer acceptability have resulted in a change in the flavor standards of the American consumer to an extent that many people doubt that beef extract could be re-introduced in the products where it has been replaced by hydrolyzed vegetable protein.

As good as these flavors are, they are a long way from the type and quality flavor needed by the Food Industry for today's expanding meat replacement market. Since marketing predictions during the 1950's projected a need for true synthetic meat flavors, industry research in this area began at this time. In 1960 the pioneering work of Batzer et al. (3) resulted in the isolation of a glycoprotein from the aqueous extract of raw beef which, upon heating in the presence of a nucleotide developed a meaty aroma. Thus, the important concept was brought forth that the basic meat aroma was due to the chemical interaction of water soluble precursors. Other investigations by numerous groups led to the conclusion that the development of meat flavor and aroma is, at least in part, due to a Maillard type reaction. As a result, raw beef has been thoroughly analyzed for its amino acid and reducing sugar content and many combinations have been formulated and subjected to various cooking conditions in an attempt to duplicate the cooked beef aroma and flavor. In an attempt to capitalize upon this basic information, a large number



ESTIMATED PRODUCTION INDICES (1970 = 100) FOR SOME MAJOR PROTEIN SOURCES (MEDIAN VALUES)

[illegible] trends in the food industry over the next twenty years.

of patents have been granted that are essentially products by process. Table 3 summarizes some of the numerous patents that have been granted in this area.

These patents are only a small percentage of the existing patents that teach the production of meat flavors by reacting water soluble ingredients. Although many of these flavors have undoubtedly enjoyed a great deal of commercial success in certain areas, they are not the final answer in meat flavors. Although flavors of this type will remain commercially viable for many years, they are essentially "stop-gap" measures until the next generation of meat flavors becomes available. In order to place synthetic meat flavors on the same level as fruit flavors, the creative flavorist must have available to him, the individual chemicals responsible for the aroma and taste of cooked beef. Only then can his creative talents be fully utilized. Thus, we find today in both the technical and patent literature a rapid movement toward the identification and utilization of individual chemicals with meat-like flavors. These are structurally different than most of the chemicals used by the flavor chemist today and entirely new synthetic and creative learning processes must evolve in order to apply and commercialize this new generation of meat flavors.

The first report of unique aromatic chemicals in boiled beef was in 1968 when Chang and co-workers (4) reported the identification of two heterocyclic compounds. These chemicals, which are shown in figure 2, are 2,5-trimethyl-delta-3-oxazoline and 2,4,5-dimethyl-1,2,4-trithiolane. Although the origin of these compounds is unknown, the oxazoline could form from the reaction of acetoin, acetaldehyde and ammonia, all of which are present during the cooking of beef. Indeed, it is synthesized in the laboratory with relative ease in this manner. The trithiolane could come from the reaction of acetaldehyde and hydrogen sulfide; however, the recent report of another new aromatic chemical in boiled beef provides a more attractive pathway. In 1972 Brinkman and co-workers (5) at Unilever, and Wilson and co-workers (6) at IFF reported the isolation of thialdine in boiled beef (figure 3). This unstable chemical will decompose to form the trithiolane during isolation and more likely during the cooking process. Thialdine could arise from the reaction of acetaldehyde, ammonia and hydrogen sulfide.

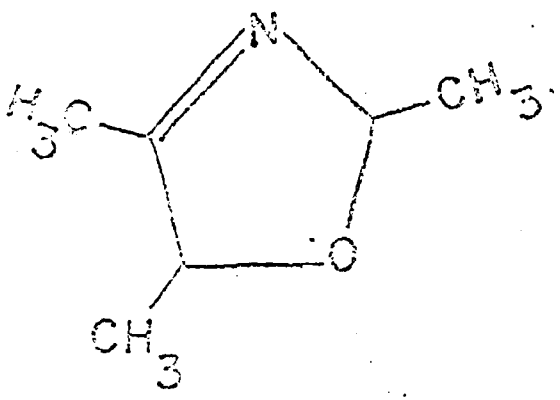
In addition to these cyclic sulfur compounds, Wilson et al. (6) reported the identification of two other new polycyclic sulfur chemicals, namely trithioacetone and trithioacetaldehyde (figure 4). Both of these chemicals were identified in cooked beef.

Other new aliphatic sulfur chemicals that have been isolated from boiled beef are 1-methylthio-ethanethiol (5), 3-methyl-2-butanethiol (6), and 2-methyl-1-butanethiol (6). Another chemical of interest is the report of 2-acetyl thiazoline in beef by Unilever workers in 1971 (7).

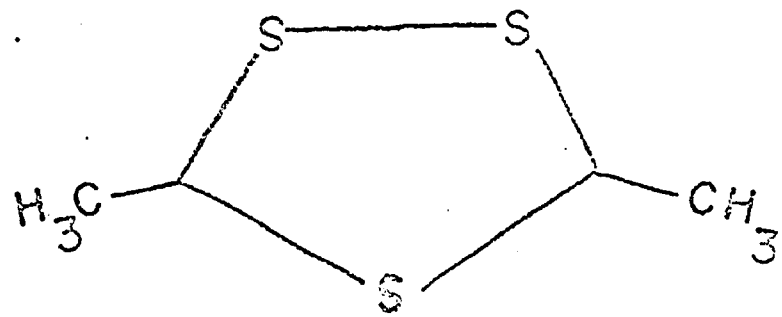
TABLE 3. PROCESSED MEAT FLAVOR PATENTS

Morton, Alkyroyd, May U.S. 2,934,437 (Lever); 2,934,436	Reducing Sugar or Glyceraldehyde + Cysteine + H_2O 120° for two hours	1960
Giacino (IFF) U.S. 3,394,015; 3,394,016	HVP + cysteine + thiamine + H_2O + heat at 110-150°	1968
Giacino (IFF) U.S. 3,519,437	Taurine + thiamine + HVP + H_2O or fat + heat + flash heating	1970
Perret, Perret and McMahon (Pfizer) U.S. 3,365,306; 3,271,167	Reducing sugars or alpha-ketobutyric acid, cysteine or methional + H_2O + heat; then add HVP and GMP and heat again for two hours	1968
Hack and Konigsdorf (CPC) U.S. 3,480,447	Amino acids (no cysteine) HVP + reducing sugar + taurine + heat 110° for 15-20 hours	1969
O'Hara, Ota, Enej, Eguchi, Okumura (Ajinomoto) U.S. 3,524,747	Amino acid (not cysteine) + lactic acid + phosphate + nucleotide-5'-phosphate	1970
Broderick and Marcus (II. Kohnstamm) U.S. 3,532,525	Cysteine + 5'=nucleotide + H_2O + heat	1970
May, Soeters (Lever) U.S. 3,532,514; 3,493,395	Reducing sugar + cysteine + fat + 70° for 24 hours or 140° until water-free	1970
Tonsbeek (Unilever) Canadian 862,685	Amino acids + lactic acid + 5'-nucleotide + heat 110-150°	1971

FIG. 2



2,4,5-TRIMETHYL- Δ^3 - OXAZOLINE

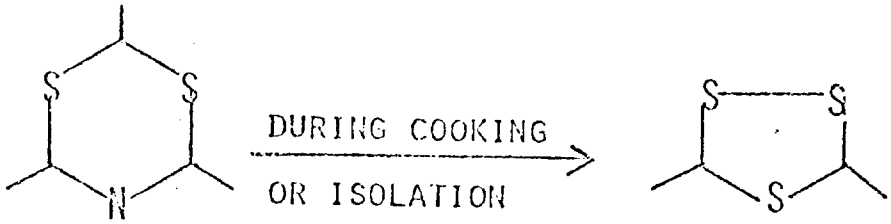


3,5-DIMETHYL-1,2,4-TRITHIOLANE

FIG. 3

POLYSULFUR CYCLICS

BRINKMAN ET AL.
(UNILEVER), 1972

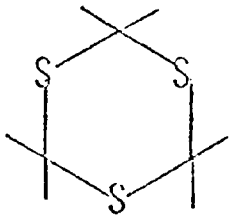


PRECURSOR PRODUCT RELATIONSHIP

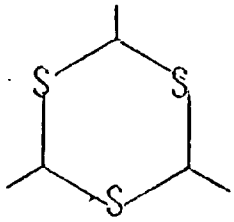
OVERALL REACTION DURING COOKING OF BEEF

$CH_3\text{-}CHO + NH_3 + H_2S \longrightarrow$ (THIALDINE) $\longrightarrow$ TRITHIOLANE

FIG. 4



TRITHIOACETONE



TRITHIOACETALDEHYDE

All of the chemicals that I have discussed were found for the first time in nature through the investigation of cooked meat flavor. Literally, hundreds of other chemicals that have been found in other heated foods such as coffee, nuts and chocolate have also been reported in beef. These include aliphatic sulfides, furans, thiophenes, thiazoles, pyrazines, aldehydes, ketones, enals and dienals.

Time does not permit me to discuss these, but certainly they are important to the creation of synthetic meat flavors.

Another group of chemicals that are important for meat flavors are chemicals that are meat-like in flavor but do not necessarily occur in beef. An awareness of these materials can only be obtained through careful reading of the patent literature. I would like to mention a few of the more interesting patents and applications.

In 1968, Tonsbeek et al. (8) reported the identification of two furanones for the first time in beef. These chemicals are shown in figure 5. Both of these chemicals are interesting flavor chemicals and the dimethyl compound was previously reported to occur in pineapple.

In 1969, IFF filed for patents on a group of furans that possess a meat-like flavor. A number of chemicals that are typical of this patent are shown in figure 6.

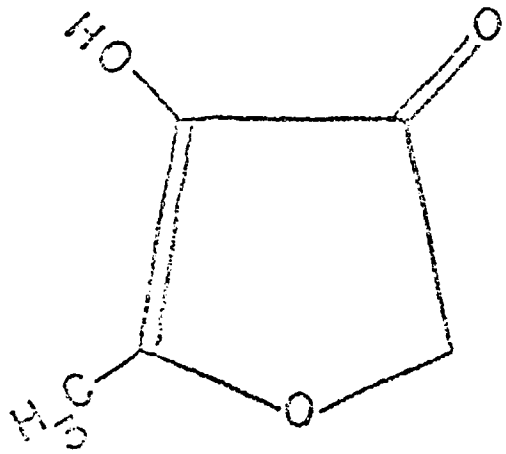
Shortly thereafter, both Unilever and IFF applied for patents that teach the reactions of the dimethyl furnanone, previously reported to occur in beef, with hydrogen sulfide to form meat flavors.

Unilever has reported (9) that the furans and thiophenes shown in figure 6 are formed as a result of the reaction. Although these chemicals and the furanthiols in the IFF patents have not been identified in meat or other heated foods, everything points to the fact that they are present and their discovery in a natural system is a challenge to the modern analytical flavor chemist.

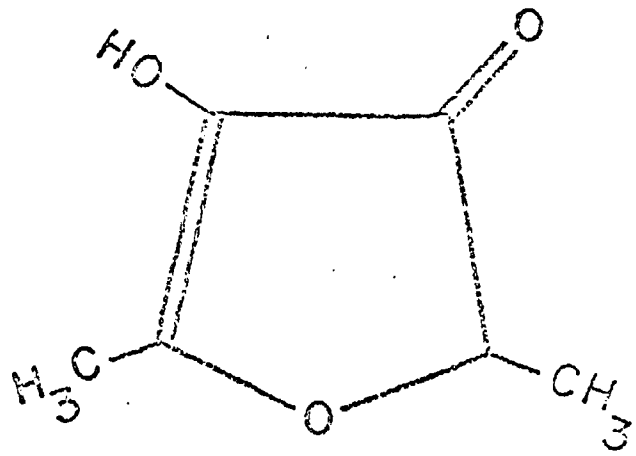
Another interesting chemical that is the subject of an IFF patent application is the discovery that dimethyl dihydroxy dithiane has a roast chicken flavor. This chemical is interesting in that it forms from mercapto acetone at ambient temperature (figure 7). The reaction is reversible upon heating and mercapto acetone is formed. The mercapto acetone and other alpha keto mercaptans have intense meat-like aromas and are the subject of other IFF patents.

In conclusion, the intense investigation of meat flavors has led to the discovery of a great number of individual chemicals that when used alone or, in combination with the previous synthetic meat flavors, will result in the creation of synthetic meat flavors that will surpass the meat flavors found on today's market.

FIG. 5



4-HYDROXY-5-METHYL-3(2H) FURANONE

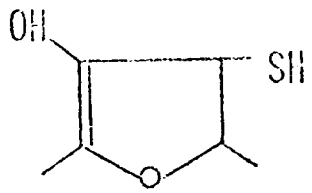


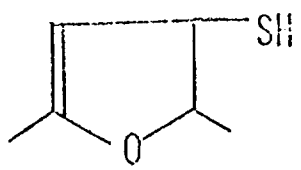
4-HYDROXY-2,5-DIMETHYL-3(2H) FURANONE

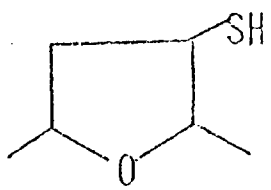
FIG. 6

MEATLIKE FURANS AND THIOPHENES

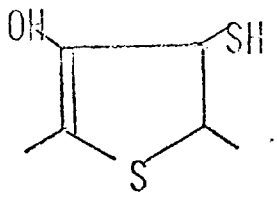
FURANS

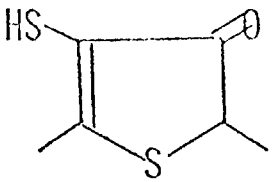


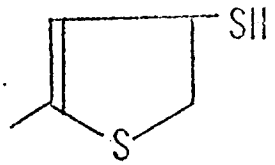




THIOPHENES







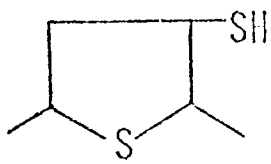
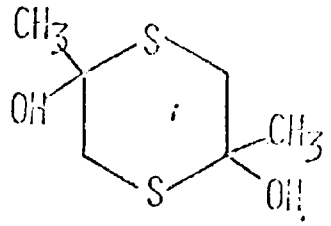


FIG. 7

ALKANE THIOLS, SULFIDES AND KETOTHIOLS

KATZ, MUSSINAN ET AL. (IFF) 1973, PATENTS APPLIED FOR

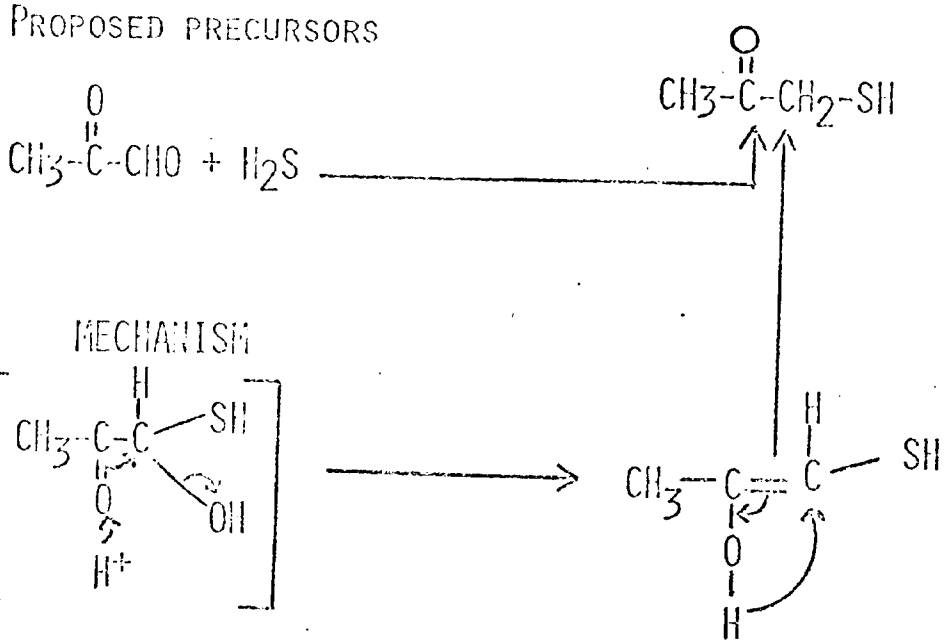


ROASTED CHICKEN FLAVOR

2,5-DIMETHYL DIHYDROXY-1,4-DITHIANE

AMBIENT ⇄ △

PROPOSED PRECURSORS



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9. van der Ouweland and Peer (Unilever) West Germany 1,932,800.

BILL SULZBACHER: I am a little bit disturbed that the cured meat flavor is due only to the antioxidant activity of the nitrites. I recall that a number of years ago when we were working on cured meats we cured some pork, lamb, rabbit and beef and gave them to our taste panel without identification and the taste panel was unable to distinguish between these meats or the species. It always seemed to me that nitrite did something specific to meat flavor; it wasn't just a matter of antioxidant activity. There was an actual contribution of nitrite to the final flavor.

Another thing occurs to me as a problem. What about corned beef, where you cure it in an essentially anaerobic manner and it isn't cured very long and you don't smoke it. You still get this very characteristic change in flavor. You can't say that it tastes anything like fresh beef. I'd like to hear this talked around a little bit and hear what other people think.

DUANE WESTERBERG: I can make just one comment along that line. There is another great factor that you put into corn beef. I know of no paper published along these lines. But what effect, actually, does seasoning have on the taste of the product? Again, eliminating some compounds such as nitrite, what does seasoning contribute to the final taste of the product?

AARON WASSERMAN: What about the effect of smoking? I think we have seen that nitrite seems to enhance smoke flavor. Have you any comments?

DUANE WESTERBERG: The only comment I have is that in some of our work when we studied antioxidants we did smoke some products with and without nitrite, at least with zero and maximum cure. We used a 5 minute smoking cycle, measured by density with GE equipment, it would be about 80%. We could actually get the flavor notes and aroma of smoke and we didn't see any difference with and without the smoke.

JAY FOX, USDA: The presence of oxides of nitrogen in the air has long been known. We have been doing some color work and without using any smoke you can get a nice beautiful pink nitric oxide color. I would like to suggest that perhaps at the low levels used to detect flavor, the presence of any type of oxides of nitrogen with the subsequent possibility of nitrite, almost any oxides you want to name, could produce enough flavor so that you wouldn't have to smoke it, nitrite it, or anything else it. Now I wonder whether this wouldn't have something to do with taste panels sometimes having a little difficulty telling whether there is an actual cured meat flavor; especially with something that has been put into a smoke house.

TOM BLUMER, NORTH CAROLINA STATE: There are several people here, I know, from Natick and they may not be at liberty to comment, but Dr. Gene Wierbicki was at our place the other day and he had something on this nitrite-nitrate flavor and I am not going to comment on it but I know about it because I tasted some of the product. I don't know whether the Natick group would be at liberty to speak on this or not.

AARON WASSERMAN: Is there anyone here from Natick that wants to answer to this? Max?

MAX BROCKMANN, NATICK: I really don't know very much about this, but it is my understanding that Wierbicki's group has observed that irradiated meat has received all the benefits of irradiation with substantially less nitrite than is normally used. I imagine that irradiation seems to compensate for a certain amount of the absence of nitrite.

AARON WASSERMAN: Well, this seems contrary--you should be getting more warmed-over flavor with all this ionizing radiation and free-radical formation. Any comments on that, Harold?

TOM BLUMER: I have one other question. How many methods would you indicate were suitable for running nitrate and nitrite. I know that this is a dynamic system and depends on what kind of product you are conducting your analysis on as to what kind of recovery you get. But there are a number of methods I know that are being used and I'd like to know which ones you think do the best job on quantitative returns.

AARON WASSERMAN: Do any of the panel have any comment on this? This is a little off the subject we are talking about. Jay, would you like to comment?

JAY FOX: We are trying to find out where nitrites go and as part of our study we ran six different methods, which come highly recommended or are in actual use, and compared them with the AOAC. We used the one which EEC (European Economic Community) is recommending or using and a few others but the best results we got were with the AOAC method. The standard deviations were essentially the same, but the highest yield was with the AOAC, and it was half again to double what the other methods gave. We also found there were some wierd discrepancies in the AOAC method, too. We have a paper coming out in the July issue of the JAOAC.

UNIDENTIFIED: Would you care to comment on the paucity of efforts on the oxidative changes in phospholipids in contrast with the enormous amount of work that has been done on the oxidation of neutral lipids?

HAROLD HERRING: Most of the work on meat off-flavor development has been on the oxidation of the phospholipid fraction. The rapidity which occurs is believed to be due to the phospholipid fraction. If one extracts, for example, meat with diethyl ether, you still get very rapid oxidation of the meat residue; if you extract with chloroform methanol the extraction removes any oxidisable lipid. I would think most of the work does indicate the phospholipid fraction in the tissue is the culprit that has been disrupted, cooked or ground.

UNIDENTIFIED: Dr. Katz showed us some data on the amount of soy protein products that are going to replace meat products and Dr. Herring had discussed rancidity development. I have a question that is going to

cut across both of these areas in the future. When we go to greater and greater substitution of meat with soy proteins it seems that the substitute is going to have to be supplemented with iron. I would like to raise the question--do we know how we are going to supplement this in terms of chemical reactions and nutritive value of the product that is produced?

IRA KATZ: I don't know; I am speculating, but one possibility may be to coat the iron to protect from its action on the food.

KEN BEERY: For Dr. Herring. On the development of the warmed flavor--apparently you have to heat it just so much to get development and if you overheat it there will be no development. What is the critical range of temperatures below which you will preclude development and above which will preclude development.

HAROLD HERRING: In our experience there is no heat below which you will have development of warmed over flavor. You have to go to sterilizing conditions to get formation of the compounds in a canning system. In a Browning reaction, products will be formed at 100°C or higher, preferably at 120°.

I believe I understood you to say earlier that you had found in deep fat fried poultry no warmed over flavor and with subsequent microwave cooking, warmed over flavor. Is this correct?

KEN BEERY: The way it was reported was that with deep fat frying then finishing off with microwave caused more development of warmed over flavor than microwave cooking up to the same temperature then finishing off with deep fat frying. The intent of the question is--are there cooking methods that could help preclude this development?

HAROLD HERRING: It may have been the deep fat frying or the time in which it was done that determined whether the initiation of the reaction occurred. And there may have been antioxidants in the deep fat frying oil which were present initially but which later may have volatilized. So one must be careful there.

KEN BEERY: Microwave cooking the entire way caused less warmed over flavor than with combinations.

HAROLD HERRING: With storage for how long?

KEN BEERY: This was a week's storage, I believe.

UNIDENTIFIED: I'd like to ask whether warmed over flavor has been confined to ground beef and if not how factors such as the size of the piece of meat, the storage in frozen condition, whether the frozen meat is wrapped in an oxygen permeable film would affect the development of this warmed over flavor? Another question, how does pork compare with beef in the development of the flavor?

HAROLD HERRING: Which pork? Fresh pork? It has been observed in our laboratory in beef, pork and poultry--turkey and chicken. Any grinding action, disruption of the cell, would expose phospholipids to the action of oxygen and catalysts. Any anaerobic packaging say, for example, with chopped beef, pre-ground beef chopped beef, does inhibit the reaction as long as it is kept anaerobic because the meat systems reduce any oxygen.

AARON WASSERMAN: We'll have time for one more question.

BOB KAUFFMAN, WISCONSIN: This is directed to Dr. Katz. I'd like to have you review for me again your projection for utilization of vegetable protein versus animal protein in the future and I do have a question to ask: Has price been considered in this prediction?

IRA KATZ: Price has been considered. Here is the projection taken from the data projected by the U.S. Department of Agriculture--Agricultural Marketing Service Report #947, Economic Research Service, USDA, 1972. The projections were one billion pounds. I don't know what aspects you are interested in.

BOB KAUFFMAN: You showed me a figure, not a table but a figure.

IRA KATZ: That was for the United Kingdom, not the United States.

BOB KAUFFMAN: Thank you, I did not understand that. What was the source of this information?

IRA KATZ: This was essentially a published survey called, "Trends in the Food Industry." I can send you the reference. Really how this was arrived at was a survey of 50 people in the food industry on what they think will happen 20 years from now or 10 years from now.