Odor and Flavor Responses to Additives in Edible Oils[1]

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ABSTRACT

The odor threshold was determined for a series of unsaturated ketones, secondary alcohols, hydrocarbons and substituted furans added to bland edible oil. Odor thresholds were taken as the point where 50% of a 15- to 18-member taste panel could detect an odor difference from the control oil. These additives are oxidative products of fats, but the concentrations investigated were far below any level associated with an identifying odor or taste of the additive per se. Odor, rather than flavor, was selected as the starting basis because of greater acuity and ease of handling a large number of samples with less taster fatigue. Oil samples containing additive concentrations near the odor threshold levels were evaluated by flavor score and flavor descriptions. Taste panel members were experienced oil tasters and were allowed free choice in selecting terms to describe the flavor quality of the oil samples. The propyl and butyl members of the homologous series of vinyl ketones had the lowest odor thresholds, whereas the difference in odor threshold was small between homologs in the unsaturated alcohols and in the 2 substituted furans. Vinyl propyl ketone, vinyl propyl carbinol (1-hexen-3-ol) and 2-propyl furan had odor thresholds of 0.005, 0.5 and 6 ppm, respectively. Odor thresholds of the unsaturated hydrocarbons are markedly lower than those of the saturated isologs. The odor of nonane can be detected at 650 ppm. However, at 1000 ppm it cannot be tasted and oils containing it were scored equal to the control oil. 1-Nonene, 1-nonyne and other tested C-9 unsaturated hydrocarbons, including a number of dienes, have odor thresholds of about 10 ppm. The hydrocarbons 1-hexyne, 1-nonyne and 1-decyne had odor thresholds of 0.2, 5 and 4 ppm, respectively.

INTRODUCTION

When it comes to taste and odor sensations, we are all distinct individualists. Only through experience with food and our environment do we gain and acquire a knowledge of taste and smell. The classification of flavor is strictly a descriptive terminology based on an individual's perception and memory. Most individuals have acute odor perception, as well as the ability to identify different aromas. Off-flavors in bland foods, for example, are often described in terms of distinctive odors rather than distinctive tastes. Descriptive terminology characterizing off-flavored fats as cardboardy, trainy, painty, skunky and rubbery illustrates the reliance on odor memory. Although odor perception has generally been regarded as being more sensitive than taste, we and others (1,2) found that when simple odorous compounds are added to fats, the taste threshold is equal to or greater than the individual's odor perception.

The contribution of saturated and unsaturated aldehydes to off-flavor characteristics of fats has been well established by many investigators (3-6). Badings (7) in his review in 1960 states that ketones are unimportant in their contribution to oxidation off-flavors. Later, Evans (8), discussing autoxidation of fats, indicated that many volatile compounds, including unsaturated esters, ketones, alcohols and hydrocarbons, arose from hydroperoxide breakdown and could contribute to an autoxidized flavor. In the past decade both vinyl amyl ketone and vinyl ethyl ketone (9-11) and their alcohol counterparts (5,9,12) have been isolated from autoxidized fats and shown to contribute undesirable flavor components.

Although various hydrocarbons have been isolated from autoxidized and irradiated fats, they reportedly have generally weak flavors. Forss (3) indicates contamination with alcohols or mercaptans as the source of hydrocarbon flavor. Smouse et al. (13) demonstrated that 1-decyne was a major component in the volatile products of slightly oxidized soybean oil. This alkyne, they stated, has a threshold of 0.1 ppm. The presence of alkynes and unsaturated hydrocarbons in autoxidized and irradiated fats has been recorded by various investigators (14-18).

The formation of alkadienes upon irradiation of beef and pork fat has been reported by Champagne and Nawar (14). They indicated that the 1-alkenes were the most highly odorous compounds of the series of alkane, alkene, alkyne and diene hydrocarbons investigated.

Chang and coworkers (19,20) isolated pentyl furan from oxidized soybean oil. They believe that this substance imparts the characteristic beany odor and flavor reminiscent of "reverted" soybean oil at concentrations of 1 to 10 ppm.

Since information on how nonaldehydic volatile components contribute to flavor is confusing and contradictory, we undertook a study to evaluate carefully the odor threshold of numerous compounds, other than aldehydes, that are products of fat autoxidation.

EXPERIMENTAL PROCEDURES

Chemicals of the highest purity available were obtained from several sources (Table I). The purity was checked by gas chromatography and all materials proved to be 98% pure or better. A number of the diene samples were purchased as special synthesis products. Some of the samples of vinyl and allyl ketones and their corresponding alcohols were synthesized in our own laboratory by the procedures of Brown and Garg (21) and of Crabalona (22).

The method of Amoore (23) and that of Patton and Josephson (24) were investigated as a technique to determine the odor threshold of several compounds dissolved in freshly deodorized cottonseed salad oil. With a 20-member panel the time involved with Amoore's method was excessive although it will give a more reproducible and accurate threshold because of its chance probability of 1 in 10. By modifying Patton and Josephson's method slightly in the plotting of taster results, the greater accuracy of Amoore's method was partially attained. Our modified procedure consists of presenting each taster with five samples, in random order, in which the minimum concentration difference between samples is twofold. The geometric scale of concentration (binary dilution) was carried out in all sets of dilutions. Samples (7.5 ml) of cottonseed oil containing the appropriate concentrations of the odorant were presented to the taster in 150 ml beakers covered with watch glasses. The samples were warmed and served at 55 C by placing the five beakers in an aluminum block heated on a thermostatically controlled hot plate. Usually one sample served as a blank, but any number of blanks

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may be used. In a preliminary run if the highest concentration was not detected by 80% of the panel, tests with higher concentrations were made. After the concentration range was established, the tests were repeated to establish an average threshold value, i.e., the point where 50% of the panel could detect the additive. In plotting the correct responses to obtain the average threshold value, only results were used of tasters who had correctly identified all the higher concentration samples. Thus the results of a taster who correctly identified the presence of the substance at concentrations of 16, 8 and 2 ppm but missed 4 and 0 parts, would be used only in calculating the percentage correct for 16 and 8 ppm. Odor thresholds are reported as the average value of two to four complete panel evaluations.

RESULTS AND DISCUSSION

The method used to determine the sensitivity threshold may be important and could account for literature differences. Threshold differences are more likely to result from taster variability and various methodologies than from minor impurities in the standards. Guadagni et al. (25) report that sniffing a water solution of nonanal was a relatively insensitive method compared to their squirt bottle method with which they attained a threshold of 1 vs. 98 ppb from sniffing. Since our odor studies were concerned with edible oil evaluations, panel methodology was the same in both odor and taste tests.

TABLE I

Detection Odor Threshold of Additives to Cottonseed Oil

Compound	Threshold,[a] ppm	Source of compound[b]
Hydrocarbons		
Alkanes		
Nonane	650	5
Alkenes		
1-Hexene	0.02	5
1-Octene	2	5
1-Nonene	9	5
1-Decene	7	5
Alkynes		
1-Pentyne	0.7	4
1-Hexyne	0.2	4
1-Nonyne	5	4
1-Decyne	4	4
Alkadienes		
1,3-Hexadiene	2	2
1,5-Hexadiene	0.5	1
cis,cis-2,4-Hexadiene	3	3
cis,trans-2,4-Hexadiene	30	3
trans,trans-2,4-Hexadiene	38	3
1,4-Heptadiene	9	3
1,3-Octadiene	20	3
1,4-Octadiene	15	3
2,4-Octadiene	12	3
1,3-Nonadiene	12	3
1,8-Nonadiene	11	3
2,4-Nonadiene[c]	9	7
Substituted furans		
2-Methyl furan	27	3
2-Ethyl furan	8	3
2-Propyl furan	6	3
2-Butyl furan	10	3
2-Pentyl furan	2	3
2-Vinyl furan	1	3
Vinyl alcohols		
1-Hexen-3-ol	0.5	7
1-Hepten-3-ol	3.0	7
1-Octen-3-ol	0.9	7
1-Nonen-3-ol	1.3	7
Allyl alcohols		
2-Nonen-4-ol	12	7
Vinyl ketone		
Vinyl methyl ketone	0.2	6
Vinyl ethyl ketone	0.02	4
Vinyl propyl ketone	0.005	7
Vinyl butyl ketone	0.007	7
Vinyl amyl ketone	0.1	7

[a] Figures have been rounded off to nearest whole number.

[b] 1, Aldrich Chemical Co.; 2, Chemicals Procurement Labs; 3, Chemical Samples Co.; 4, K&K Labs; 5, Phillips Petroleum Co.; 6, Chas. Pfizer & Co.; and 7, synthesized.

[c] A 50:50 mixture of 1,3- and 2,4-isomers.

Table I shows the odor detection threshold for a series of hydrocarbons, substituted furans, unsaturated ketones and alcohols. Because thresholds of saturated aliphatic hydrocarbons range about 1000 ppm, these hydrocarbons were not a part of our study. Unsaturation confers a high odor potential to aliphatic hydrocarbons. Detection limits are lower by an order of two to three magnitudes from the saturated analogs. A triple bond lowers the threshold more than a double bond and from limited data the difference can be as much as one order of magnitude. Sometimes, dienes have had significantly lower thresholds than monoenes of the same carbon chain length. No consistent effect of conjugation, nonconjugation or terminal position of the double bonds could be observed with the limited number of samples investigated. In the series of 2,4-conjugated hexadienes, the *cis,cis*-geometrical isomer could be detected at 1/10 the concentration of either the *cis,trans*- or the *trans,trans*-isomer.

Odor thresholds of less than 1 ppm are indicated for a number of hydrocarbons, and apparently the six-carbon chain homolog has the lowest threshold in each series. Trace amounts of unsaturated hydrocarbons near these threshold levels could modify the flavor response for any fat or fatty food where they may be present.

Odor thresholds of 2-substituted furans are, in general, comparable to the odor threshold levels of unsaturated hydrocarbons. If furans are products of autoxidation (20), it would also be logical to expect the formation of unsaturated furans. The odor threshold of 2-vinyl furan was determined to be 1 ppm.

The more polar vinyl alcohols and ketones have much lower odor thresholds than the nonpolar hydrocarbons. The odor thresholds of the vinyl ketones were found to be in parts per billion, which range agrees with values reported in the literature (4,10,26). Unsaturated ketones have a much stronger odor, which can be detected at concentration levels 1/10 to 1/100 of that of their alcohol analogs. The detection odor threshold of the unsaturated ketones is in the range of our most potent odorous materials, the sulfides. Hydrogen sulfide has an odor threshold of 12.7 ppb and methyl mercaptan in water, of 2 ppb (24).

In Table II are presented the flavor responses of various hydrocarbons dissolved in freshly deodorized cottonseed oil. The samples have been evaluated against a bland control oil and have been given both a flavor score and a flavor description. Taste panel operation was conducted by the method of Moser et al. (27). Flavor descriptions are considered predominate only when 25% of the taste panel members indicate the presence of a particular flavor. Similar flavor responses may be given by 75% of the panel members, but rarely is it found that all tasters in a 20-member panel will give identical flavor responses. Hydrocarbons at low levels definitely influence the flavor but do not convey a "gasoline" or hydrocarbon type of odor to edible oils. The usual pattern is an increase of the rancid responses, which increase with concentration of the additive. The flavor responses are still typical of fats, even though the level of addition of the more odorous alkynes may be sufficient to give low scores indicating repulsive flavors. A few rubbery and melony responses were occasionally observed with the hydrocarbons. Although such comments are not uncommon, they do not constitute the

TABLE II

Taste Responses of Hydrocarbons Added to Bland Cottonseed Oil

Hydrocarbon	Concentration, ppm	Flavor score[a]	Flavor responses
Nonane	1000	6.5 +	Buttery, beany
Nonane	2000	5.7 *	Grassy, unknown
1-Nonene	4	6.1[b]	Buttery, nutty, rancid
1-Nonene	8	5.8	Buttery, rancid, nutty
1-Nonene	16	5.3	Rancid
1-Nonene	32	4.7	Rancid
1-Hexyne	0.5	3.2**	Buttery, rubbery
1-Decyne	5	4.8**	Buttery, beany
1-Decyne	10	5.0**	Buttery, grassy, melony
1,3-Nonadiene	8	6.7[b]	Buttery, rancid, beany
1,3-Nonadiene	16	6.3	Buttery, rancid
1,3-Nonadiene	32	5.1	Buttery, rancid
1,3-Hexadiene	5	5.7**	Buttery, rancid
Cottonseed oil	—	7.2-8.5	Buttery, nutty

[a] Where significance is indicated, the sample was compared to cottonseed oil; 3, no significance at the 5% level, *, significant at the 5% level, **, significant at the 1% level.

[b] Comparisons within the group.

predominant descriptions given to aged edible oils. No atypical flavor response was observed in any tests with the hydrocarbons. Taste panel responses would indicate that when hydrocarbons are present the odor and taste descriptions fit into the normal flavor profile of aged fats.

The taste responses shown in Table III to vinyl alcohols added at levels slightly above their odor threshold were in our experience atypical to aged edible oils. Rubbery is a predominate flavor response; musty, foreign, unknown and even hydrocarbon descriptions have completely displaced the usual edible oil flavors. Flavor evaluation studies conducted at lower vinyl alcohol concentrations may change these responses considerably.

1-Octen-3-ol, isolated from oxidized lipids (5,12), reportedly contributes to the mushroom odor of dairy fats. In butterfat its flavor threshold is 0.1 ppm. 1-Penten-3-ol, isolated from milk fat and meat, has an oily, grassy flavor (3).

2-Pentyl furan has a flavor threshold of 1 ppm and a flavor reminiscent of reverted soybean oil (20). Repeated tests by our panel using Amoore's method indicate that no taster could consistently identify by odor (three out of three tests) samples containing 2-pentyl furan below levels of 4 ppm. When the panel used Patton and Josephson's technique, the average of three tests gave the 50% detection threshold at 2.4 ppm. When 1 to 20 ppm of 2-pentyl furan were tested in freshly deodorized cottonseed oil, taste panel results indicated that levels of approximately 5 ppm gave typical aged oil responses. At levels of 1 ppm the samples were no different than the control. At 20 ppm the licorice odor of the pure material could be detected by several panel members. Mildly oxidized flavor responses were obtained at 5 and 8 ppm of 2-pentyl furan. Additions at these levels significantly lowered the flavor score, as shown in Table IV. Cottonseed oil containing 8 ppm of 2-pentyl furan was scored significantly higher than aged soybean oil. A sample containing 5 ppm of 2-propyl furan was not scored significantly below the control cottonseed oil. The flavor responses are not greatly different from those obtained with the various unsaturated hydrocarbons. Although the responses are reminiscent of mildly oxidized oils, we do not interpret the responses of either the hydrocarbons or the 2-pentyl furan as being unique for aged soybean oil, i.e., what makes its flavor different from cottonseed, etc.

The odor and taste properties of the furan compounds would be of considerable interest to fat technology if proof of their origin from autoxidized fats could be unequivocally established. Nonaka et al. (28) reported the presence of seven homologs, methyl to heptyl, of 2-alkyl furans in the aroma volatiles of cooked chicken. Those authors postulated two sources for the furans and indicated that there was no reason to assume they were artifacts of contamination, although this possibility could not be totally excluded. Those authors found that *n*-butyl furan and *n*-pentyl furan were among the oxidation products of *trans,trans*-2,4-decadienal. Since several dienals have been reported in autoxidized fats, the dienals on further oxidation could be the source of a homologous series of furans. The other proposed source was from glucose through reactions similar to the pyrolysis of sugars. A large series of furan derivatives has been detected in a concentrated coffee aroma obtained by molecular distillation of expelled coffee oil (29). The source of furans was attributed to condensation within the carbohydrates during roasting of the green coffee bean.

Historically, oxidative off-flavor development in edible fats has been concerned with the development of aldehydes, to almost the complete exclusion of other oxidatively derived substances. There are many reasons for this attitude, and early flavor studies were confined to aldehydes not only because they were present in larger quantities, but primarily because solid derivatives could be made and handled and because the products could be identified. Improved techniques soon allowed the separation of unsaturated classes of aldehydes and the observance that certain fractions contained ketones and perhaps dialdehydes. Many workers have emphasized the difficulty of obtaining derivatives and the instability of vinyl ketones in a gas chromatograph.

The free radical nature of autoxidation and the randomness of chain splitting, as breakdown products are formed, make it absurd to assume that a single compound or a few stable ones, first isolated and identified by chemists, are the

TABLE III

Flavor Evaluation of Vinyl Alcohols Added to Cottonseed Oil

Compound	Flavor score[a]	Flavor responses
1-Hexen-3-ol, 2 ppm	2.5**	Rubbery, rancid, hydrocarbon
1-Hexen-3-ol, 4 ppm	2.7**	Rubbery
1-Octen-3-ol, 2 ppm	4.7**	Musty, foreign, unknown
Cottonseed oil	7.1-7.5	Buttery

[a] See footnote for Table II.

TABLE IV

Flavor Evaluation of 2-Pentyl Furan in Cottonseed Oil

Compound	Odor score[a]	Flavor score[a]	Predominant flavor responses
2-Pentyl furan, 1 ppm	8.4-8.6 +	—	Bland, buttery
2-Pentyl furan, 1 ppm	—	6.7 +	Buttery, beany
2-Pentyl furan, 5 ppm	7.2-7.8 **	—	Buttery, grassy
2-Pentyl furan, 5 ppm	7.1 +	5.5*	Buttery, rancid
2-Pentyl furan, 5 ppm	6.6*	5.5**	Rancid, buttery, grassy
2-Pentyl furan, 5 ppm	—	6.3*	Rancid, grassy
2-Pentyl furan, 8 ppm	7.2	6.0[b]	Rancid, grassy, buttery
2-Pentyl furan, 8 ppm	6.6	5.5[b]	Rancid, buttery
2-Pentyl furan, 20 ppm	6.5**	—	Grassy, rancid
Cottonseed oil	8.7-9.2	7.0-7.3	Buttery

[a] See footnote for Table II.

[b] Compared with aged soybean oil.

only source of odor and flavor. Hammond and coworkers (4,11) and Day et al. (30) recognized that although a single compound could produce the predominate flavor response, it was only after a blending of several odorous compounds (aldehydes and ketones) that the flavor was more similar to the natural autoxidized flavor of oxidized milk or aged soybean oil. The problem of simulating a natural odor is further complicated by the antagonistic effect reported by Meijboom (2) where two compounds, one having an odor threshold of 0.1 ppm, the other at 10 ppm, can be mixed at levels of 13.2 and 12.5 ppm, respectively, in paraffin oil to give an odorless and almost tasteless mixture. In his review on palatability Tilgner (31) indicates that 20 to 50 chemical compounds may be combined to produce a typical aroma and flavor, but that the number of compounds in the original material may total in the hundreds or even thousands.

Because of its high resolving power gas chromatography has been the favorite tool of the flavor chemist. A more sophisticated technique, obtained by combining a gas chromatograph directly to a mass spectrometer, has again markedly revealed the myriad of compounds that occur in the aroma volatiles of foods. Using a tandom gas chromatograph-mass spectrometer unit Nonaka et al. (28) identified 62 compounds in chicken meat volatiles of which only 13 were previously known. At least eight aromatic hydrocarbons have been reported in volatiles of the potato (32), and the known aroma volatiles of coffee have increased to more than 200 compounds (29). Similar increases in the number of aroma volatiles can be shown for almost any food where the volatiles have been investigated by a gas chromatograph-mass spectrometer unit.

Many unsaturated and easily oxidized odor volatiles are never detected because they are lost during isolation or fractionation in a gas chromatographic column. The distinct limitations in capability of gas chromatography to handle unstable materials is ignored or overlooked in much odor and flavor work. It is of the utmost importance to recognize that compounds issuing from a chromatographic column are not necessarily all that were injected. Improved techniques in odor studies will further increase the number of these fugitive aroma compounds.

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