The Flavor Intensity of Some Carbonyl Compounds Important in Oxidized Fats

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ABSTRACT

The flavor intensities of several methyl ketones, aldehydes, 2-enals, and *trans,trans*-2,4-dienals were evaluated in 1% mineral oil in water emulsions against a series of standard emulsions of 2-heptanone. There was a linear relation between the logarithm of the concentrations of the carbonyls and the logarithm of the concentration of 2-heptanone giving an equal flavor intensity. Thresholds calculated from these linear relations were comparable to those reported in the literature. Mixtures of carbonyls similar to those found in oxidized soybean oil were evaluated, and their flavor intensities were similar to those predicted from adding the intensities of the individual carbonyls. The flavor intensity of these carbonyls could account for the flavor intensity of oxidized soybean oil.

INTRODUCTION

The oxidation of fats and oils gives rise to a myriad of flavor compounds among which carbonyl compounds are prominent (1). In attempting to evaluate the relative importance of these flavor carbonyls, investigators frequently have measured flavor thresholds. These have been reported in various media because thresholds depend on the medium in which compounds are examined (2-8). It often is assumed that compounds present in concentrations above threshold contribute to the flavor, and the relative importance of a compound in the flavor is related to the ratio of its concentration to its threshold concentration (9).

Stevens found that the sensory magnitudes of various stimuli were power functions of their physical magnitudes (10,11), and thus, the flavor or odor intensity of a compound is related to its concentration by the equation

$$S=aC^b$$

or

$$\log S = \log a + \log C$$

where S is the sensory intensity, C is the concentration and a and b are constants. It follows from these equations that if the sensory intensities of two compounds are compared with each other, the concentrations of the two that have equal sensory intensity are related by the equation

$$\log C_1 = \log[(a_2/a_1)]/b_1 + b_2/b_1 \log C_2$$

where the subscripts 1 and 2 refer to compounds 1 and 2, respectively. Thus, $\log C_1$ is a linear function of $\log C_2$ with a slope b_2/b_1. Moskowitz et al. (12) proposed choosing n-butanol as a standard odor source and using this equation for making comparisons. They pointed out that this allowed comparisons of results from different laboratories and would make it possible to express odor control regulations in terms of a readily available standard. A great deal of data has been correlated with this equation with a butanol standard (13).

Use of these equations has demonstrated that compounds can differ considerably in the values of the equation constants a and b. This means that the sensory intensity of a compound at concentrations above its threshold is not predictable from its threshold concentration.

The sensory intensities of mixtures of odor compounds also have been investigated. Frequently the sensory intensity of a mixture is not simply the sum of the intensities of the components, but no predictive generalization is available (14,15).

Recently Stone and Hammond developed a method of evaluating the flavor intensities of fats and oils in emulsion (16). This method has the advantage of allowing examination of multiple samples without the usual carryover that occurs when oils are tasted directly. It allows the multiple comparisons necessary to compare the flavor intensity of oil-soluble compounds with a standard. We have used this method to compare the flavor intensities of several homologous series of carbonyl compounds with a standard to establish their relative importance in the flavors of oxidized fats and oils.

METHODS

Carbonyls: All carbonyls were purchased commercially. Those that were considered polymerized were distilled through a 40-cm Widmer column under reduced pressure and sealed in glass for storage at 2 C. The purity of the carbonyl compounds was tested on a Varian 3440 Gas Chromatograph (Palo Alto, California) equipped with a 3-M × 0.3-cm column packed with 10% OV 225. Two microliters of each carbonyl dissolved in 1 mL of hexane was injected. If only one peak was observed from the compound, it was considered free of volatile impurities. To verify the absence of nonvolatile impurities, each ketone was mixed with a weighed amount of the ketone of next greatest chain-length. If the areas under the peaks corresponded to the relative percentages, the ketones were considered free of nonvolatile impurities. Other carbonyls were evaluated similarly except the ketone of corresponding chain length was used to verify the absence of nonvolatile impurities.

Emulsion preparation: Water was prepared according to Stone and Hammond (16). Mineral oil was Sontex 35 white USP grade (Sontex, Dickenson, Texas). A blank emulsion was prepared by blending 10 g of gum acacia with 1,600 mL of water for 30 sec at medium speed of an Oster Pulse Matic blender (John Oster, Inc., Milwaukee, Wisconsin). After 30 sec, 16 mL of mineral oil (sontex 35, USP white, Sontex, Dickenson, Texas) was added, and blending was continued for 1 min.

Standard emulsions were prepared from mineral oil solutions containing 4, 2, 1, 0.5 and 0.25×10^{-4} parts by volume of 2-heptanone. Gum acacia and 800 mL of water were blended for 30 sec, and then 8 mL of one of the 2-heptanone solutions were added.

Carbonyl compounds to be compared with 2-heptanone were prepared at concentrations in mineral oil perceived by the panel operator as being in the correct range. Four concentrations were prepared in which each successive concentration was threefold more concentrated than its predecessor. The mineral oil solutions were emulsified, as were the standards. If these emulsions did not have flavor intensities in the range of the standards for most judges, the concentration was adjusted.

The emulsions were evaluated in isolated booths at room temperature. During the course of the experiment 16 persons participated in the evaluation of the flavor intensities. At individual sessions usually 10 to 12 persons participated. The standards were labeled A through E in order of increasing concentration; the samples were identified by random numbers. The panel members were instructed to swirl each emulsion before tasting it. They were advised to place the sample emulsions in order of increasing intensity by their odor and to begin comparison with the most dilute. They were instructed to rinse their mouths out with blank emulsion between samples. The panel was to place each sample as being equal in intensity to one of the standards or in between two of the standards. Samples that were more or less intense than any of the standards were to be so indicated. Blank emulsions or duplicate dilutions of the compound being tested were included at random among the sample emulsions. After they had evaluated the samples, panel members were informed of the correct order of increasing concentration for the samples and which were blanks or duplicates.

Because of individual variation in perception it seldom was possible to present samples that did not exceed the range of the standards for some judges. It was necessary to decide how such data and values that fell between standards were to be averaged in with the rest of the observations. The following rules were adopted: When an observation was reported as being between two standards, the average arithmetic concentration of the two standards was calculated for the value of the standard having equal flavor intensity. When a sample was reported as being less intense than standard A, that judge's observation was not recorded because A was the threshold. When 40% or more of the judges reported a sample as less than standard A in intensity, no observations were recorded for that sample. When a sample was reported as being more intense than standard E, a logarithmic value of −5.22 was recorded. This corresponded to the logarithm of the arithmetic average of the concentration of standard E and the next highest possible standard (twice the concentration of E). Such a standard was not actually used because studies indicated that it was so intense as to be offensive to most of the panel. If two or more samples were reported more intense than standard E by a panel member, then the weakest of them was given a value of −5.22 and the rest were not recorded. Data from a judge were used only when the increasing order of concentration had been correctly identified.

The panel was trained initially by judging samples of 2-heptanone against a 2-heptanone standard. The correctness of such evaluations could be determined by the log-log plots giving a slope of ∿1 and an intercept of ∿0. Such checks on the panel were applied periodically and when the panel was inactive for several weeks. At first there was a strong bias to rate samples so that they fell within the range of the standards whether this was appropriate or not. This bias was overcome by presenting samples of 2-heptanone that were outside the range of the standards and informing the panel members of the strength of the samples after their evaluation. The inclusion of random blank and duplicate samples also served to monitor panel performance and make sure they were relying only on sensory clues. No panel members were rejected for inability to make the comparisons once proper procedures and safeguards were instituted.

The threshold of 2-heptanone in emulsion was determined in a triangle test with 12 observers. The threshold was used for the concentration of standard A, the most dilute standard.

RESULTS

We did not use n-butanol as a standard (12) because it is too water soluble to make a good standard for emulsions. 2-Heptanone was chosen as a standard because it is readily available in a pure form and is known to occur in foods (17). A ketone was preferred because they are the most stable of the carbonyls.

Figure 1 shows typical log-log plots of the concentrations of various ketones having the same flavor intensity as concentrations of 2-heptanone. Table I shows the statistically-fit slopes and intercepts of such plots for all the

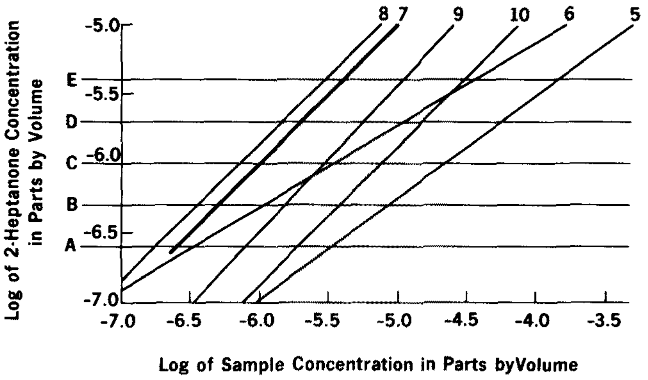

FIG. 1. Log-log plots of the concentration of 2-heptanone perceived to have the same flavor intensity as various concentrations of 2-ketones with chain lengths 5 to 10. The points A through E are the concentrations of the standards given the panel. A is at threshold and each successive standard is twice as concentrated as its predecessor.

TABLE I

Slopes, Intercepts, Correlation Coefficients and Panel Average Standard Deviation for Linear Fits of Log-Log Plots of the Concentrations of 2-Heptanone Perceived to have the Same Flavor Intensities as Various Concentrations of Carbonyl Compounds

Compound	Slope	Intercept	R^2	Panel Av. std. dev.
2-pentanone	0.95	−1.58**	0.62	$0.189^{b,c,d}$
2-hexanone	0.67**	−2.29**	0.72	$0.165^{a,b}$
2-heptanone	1.05	+0.26	0.83	0.118^{a}
2-octanone	0.92	−0.31	0.56	$0.210^{b,c,d,e,f}$
2-nonanone	1.08	−0.05	0.52	$0.269^{e,f,g}$
2-decanone	1.01	−0.85	0.52	$0.218^{b,c,d,e,f}$
3-heptanone	0.60*	−2.67*	0.34	$0.261^{d,e,f,g}$
4-heptanone	0.78	−1.60*	0.55	$0.207^{b,c,d,e,f}$
oct-1-en-3-one	0.54**	−3.20**	0.52	$0.227^{b,c,d,e,f}$
pentanal	0.73*	−2.32**	0.50	$0.251^{c,d,e,f,g}$
hexanal	0.65**	−2.26**	0.51	$0.251^{c,d,e,f,g}$
heptanal	0.48**	−2.92**	0.39	$0.265^{d,e,f,g}$
octanal	0.45**	−3.30**	0.43	$0.282^{f,g}$
nonanal	0.29**	−4.33**	0.20	$0.250^{c,d,e,f,g}$
decanal	0.27**	−4.51	0.16	$0.276^{e,f,g}$
2-hexenal	0.67**	−2.01**	0.54	$0.225^{b,c,d,e,f}$
2-heptenal	0.67	−1.67	0.41	0.320^{g}
2-octenal	0.55**	−2.72**	0.69	$0.183^{b,c}$
2-nonenal	0.56**	−2.79**	0.59	$0.213^{b,c,d,e,f}$
2-decenal	0.52**	−3.39**	0.45	$0.284^{f,g}$
t,t-2,4-hexadienal	0.86	−1.20*	0.68	$0.200^{b,c,d,e}$
t,t-2,4-heptadienal	0.41**	−3.58**	0.32	$0.199^{b,c,d,e}$
t,t-2,4-octadienal	0.46**	−3.47**	0.45	$0.232^{b,c,d,e,f}$
t,t-2,4-nonadienal	0.31**	−3.98**	0.35	$0.259^{d,e,f,g}$
t,t-2,4-decadienal	0.42**	−3.82**	0.48	$0.283^{b,c,d,e,f}$

[*,**] Indicate a significant difference from slope 1.0 and intercept 0.0 at 95% and 99% confidence. The panel standard deviations are for the logarithm of the 2-heptanone concentration, values which ranged from −5.4 to −6.6. Panel standard deviations having a letter in common are not statistically different. Note that this is the average of the panel standard deviation and not the standard deviation of the panel mean.

carbonyl compounds evaluated. The fit was not improved by nonlinear equations.

None of the slopes for the 2-ketones except 2-hexanone was statistically different from 1 and none of the intercepts was significantly different from 0 except those for 2-pentanone and 2-hexanone. Ketones with the carbonyl group further from the end of the carbon chain had lower slopes and intercepts than those of the 2-ketones. The slopes and intercept of the carbonyl compounds other than 2-ketones generally were significantly less than 1 and 0, respectively. For both the saturated and unsaturated aldehydes, there is a tendency for the slope and intercept to decrease with chain length.

The R^2 values, which report the variability accounted for by linear regression, are greater with ketones than the other carbonyls and greatest of all for 2-heptanone, the standard. The lowest R^2 values are associated with the least slopes, partly because the variation in the data attributable to regression becomes smaller in these instances.

The standard deviation of the panel for an observation may be used as a statistic to gauge panel performance. The smaller the standard deviation, the better the performance. To see if the panel performance varied with the compound being tested, the standard deviations were calculated for each observation. An analysis of variance of these values showed that the panel performance varied significantly with the compound being evaluated. Table I shows the mean of the standard deviations for each compound tested and a test of the least significant difference among them. The standard deviation of the panel is least for 2-heptanone. This suggests that the panel does best at evaluating 2-heptanone against itself and does better in evaluating compounds of similar flavor to 2-heptanone. The panel performance was worst with n-aldehydes.

From the data in Table I, the concentration of each compound that has a flavor intensity equal to the five 2-heptanone standards may be calculated. These values for the various chain lengths of each class of compounds are expressed graphically in Figures 2-5. These curves are symmetrical for the ketones and 2-enals so that minima are found at 2-octanone and 2-heptenal. For saturated aldehydes and 2,4-dienals, the curves are less regular, especially the C9 and C10 points. Minima are observed at nonanal and 2,4-nonadienal. The ordinate is logarithmic, SO −6 corresponds to a concentration of 1 ppm and −7 to 0.1 ppm, etc. The aldehydes generally require less concentration to give a particular flavor intensity than the ketones of the same chain length. Greater amounts of a dienal are required to give the same flavor intensity as aldehydes of the same chain length, except for C9. The enals have flavor intensities similar to the aldehydes at C6, C7, and C8 but deviate at C9 and C10.

The value for the A standard represents the threshold of 2-heptanone in emulsion. This was verified by the fact that at panel sessions approximately half the panel reported that they could not taste the A standard. This means that the A-values for the other compounds are also at threshold. This procedure constitutes a simple and reliable way to establish threshold values (12). The threshold values obtained in this way are compared with those reported in the literature in Table II. Values of thresholds for a particular compound in the literature frequently differ by an order of magnitude or more, and usually our emulsion values agree this well with one of the literature values. Generally thresholds are greater in oil than in water (2,5). It is not clear how these should be related to thresholds in emulsion. Since we considered only carbonyls with a chain length of five or more, the compounds are much more soluble in oil than water. In 27 out of 33 instances, the emulsion threshold was less than reported values for oil. In 12 out of 15 in-

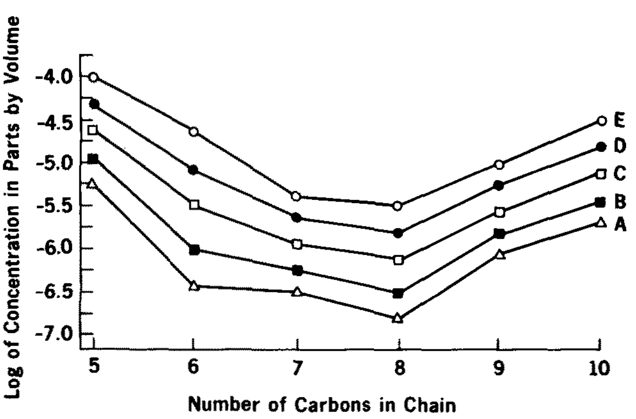

FIG. 2. Concentration of 2-ketones having flavor intensities equal to those of the five 2-heptanone standards, A through E.

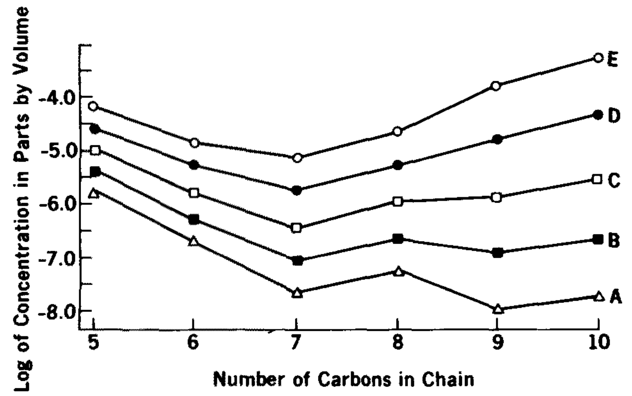

FIG. 3. Concentration of n-aldehydes having flavor intensities equal to those of the five 2-heptanone standards, A through E.

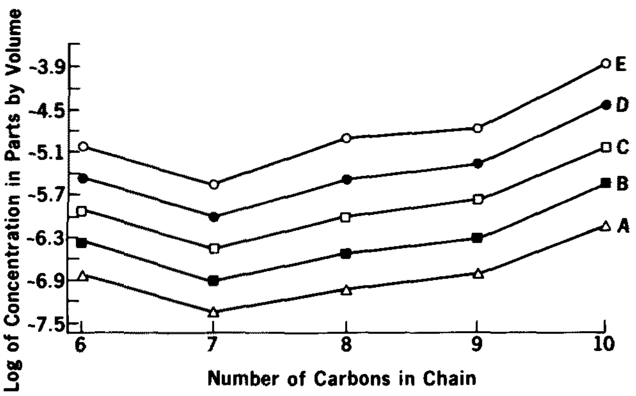

FIG. 4. Concentration of 2-enals having flavor intensities equal to those of the five 2-heptanone standards, A through E.

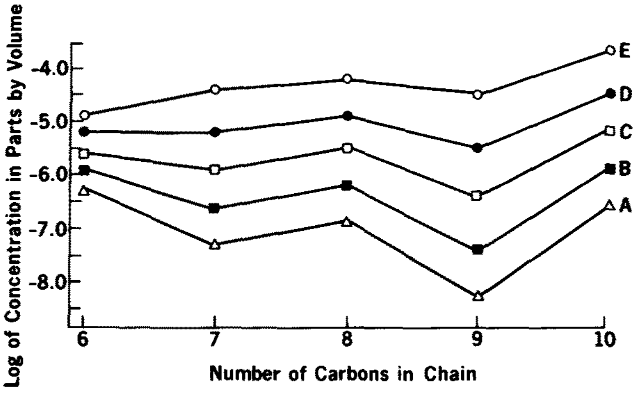

FIG. 5. Concentration of *trans,trans*-2,4-dienals having flavor intensities equal to those of the five 2-heptanone standards, A through E.

TABLE II

Flavor Thresholds in Parts Per Million of Emulsion Calculated from Our Evaluations in Mineral Oil-Water Emulsion Compared with Values in the Literature in Various Media

Compound	Oil-water emulsion	Oil	Water	Milk
2-pentanone	5.5	61(5)		
2-hexanone	0.38			
2-heptanone	0.31[a]	15(5)	1(7)	
2-octanone	0.16	2.5(5),12(2),3.5(2)	0.15(5),1.6(2)	
2-nonanone	0.81	7.7(5)		
2-decanone	1.9	11(5)	0.19(5)	
3-heptanone	0.26			
4-heptanone	0.38			
oct-1-en-3-one	0.50		0.01(7)	
pentanal	1.4	0.15(4),0.30(5)	0.07(5),0.08(7)	0.13(3)
hexanal	0.19	0.15(4),0.19(5) 0.3(2),0.6(2)	0.016(5),0.02(7) 0.03(2),0.3(7)	0.05(3)
heptanal	0.019	0.042(4),0.75(5)	0.031(5)	0.12(3)
octanal	0.045	0.068(4),0.6(2) 0.9(2),0.9(5)	0.005(2)	0.46(3)
nonanal	0.011	0.32(4)		0.22(3)
decanal	0.015	0.6(2),0.7(2),1.0(4)	0.007(2)	0.24(3)
2-hexenal	0.15	2.5(4)		0.067(3)
2-heptenal	0.042	0.63(4)		0.077(3)
2-octenal	0.083	1.0(4)		
2-nonenal	0.14	0.08(2),0.1(4) 0.4(2)	0.006(2)	0.004(3)
2-decenal	0.71	5.5(4)		0.092(3)
t,t-2,4-hexadienal	0.53	0.036(4)		
t,t-2,4-heptadienal	0.045	0.46(4)		0.049(3)
t,t-2,4-octadienal	0.14	0.15(4)		
t,t-2,4-nonadienal	0.005	0.46(4)		
t,t-2,4-decadienal	0.26	0.28(4)		

[a] Direct measurement value was 0.25.

stances, the emulsion threshold was greater than reported values for water. Presumably the emulsion data should be more comparable to values reported for milk. In 5 out of 11 instances the emulsion threshold was greater than those reported for milk.

Meijboom (4) reported that the thresholds of 2-enal and 2,4-dienals alternated for odd and even chain lengths so that odd carbon 2-enals had lower thresholds than even. For 2,4-dienals even chains had lower thresholds. Our data show some alternation but do not support Meijboom's generalizations.

Figure 6 shows the limitations of depending on threshold values to predict flavor significance at values above the threshold. The figure shows that 2-heptanone and 2,4-heptadienal have similar thresholds, 0.31 and 0.26 ppm, respectively. For these two compounds to be perceived as equally intense at the intensity of standard E, the concentration of 2-heptanone must be increased 16-fold, but that of 2,4-decadienal, 708-fold. Thus at the intensity of standard E, 2-heptanone is 44 times more intense than 2,4-decadienal. In general, unless compounds have similar slopes in log-log plots, threshold values do not predict their relative importance at higher concentrations (9).

The carbonyls evaluated are believed to be important in the flavor of oxidized fats and oils. It is not clear from the data in Table I how the flavor intensity of these compounds will behave in mixtures or if they can account for the flavors of oxidized oils and fats. White and Hammond (18) recently reported the analysis of carbonyl compounds in soybean oil oxidized at 55 C for 3, 5 and 8 days. These values are given in Table III. Mixtures of the carbonyls were made in mineral oil at their reported concentrations, and the flavor intensity of the mineral oil solutions was evaluated in emulsion against the 2-heptanone standards. One also can calculate the flavor intensity that such a mixture should give from the data in Table I if one assumes that the flavor intensities of all the components are simply additive. The panel results are compared with the predicted additive flavor intensities in Figure 7. The sample representing the oil oxidized 8 days at 55 C had to be diluted 80-fold to get it to fall within the intensities of the 2-heptanone scale. Dilutions of the mixtures representing 3 and 5 days also were evaluated. The simple additive model predicted a flavor intensity that was a fair estimate of the observed intensity. There is a tendency for the predicted values to be lower than those actually observed. This is in agreement with observations on the intensities of simple odor mixtures which usually are not simply additive (14, 15). The flavor character of the mixtures was reminiscent of that of oxidized soybean oil, but it is our opinion that it would be easy to distinguish the synthetic mixtures from

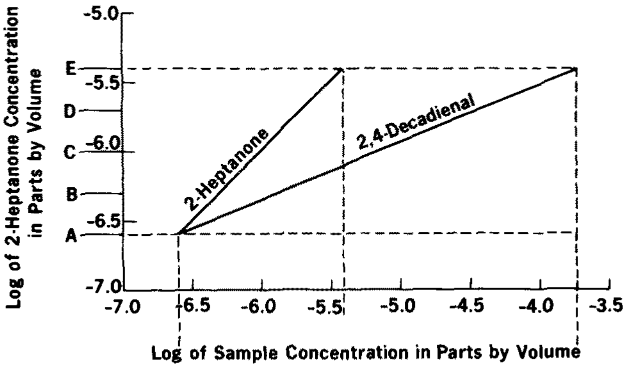

FIG. 6. A log-log plot of the concentration of 2-heptanone equal in flavor intensity to various concentrations of *trans,trans*-2,4-decadienal. Although the two substances have similar thresholds, the amount required at an intensity equal to standard E is quite different.

TABLE III

Amounts (ppm) of Carbonyls Found in Soybean Oil Oxidized at 55 C[a]

Carbonyl	Day P.V.	3 1.4	5 9.3	8 16.3
pentanal		–	0.16	3.5
hexanal		2.4	35	45
octanal		0.94	2.0	2.0
nonanal		–	6.4	10
decanal		0.39	1.1	1.6
2-hexenal		1.2	6.9	9.9
2-heptenal		0.61	3.5	5.5
2-octenal		–	6.4	10
2-nonenal		0.39	1.1	1.6
2-decenal		–	–	0.42
2,4-hexadienal		0.42	1.1	1.3
2,4-heptadienal		–	0.90	1.6
2,4-octadienal		–	0.81	1.1
2,4-nonadienal		–	2.9	6.9
2,4-decadienal		0.14	0.48	0.73

[a]2-Pentenal also was reported, but 2-pentenal was too water soluble to be evaluated by our method.

oxidized soybean oil. This may be because the synthetic mixtures do not contain *cis-trans*-isomers of the 2-,4-dienals and other components such as vinylethyl ketone, diacetyl, 3-*cis*-hexenal, and 2-pentylfuran. Even without these compounds, the flavor intensity of these mixtures is comparable to soybean oils oxidized for similar times (16), and it seems that these carbonyl compounds are able to account for the flavor intensity of oxidized soybean oil.

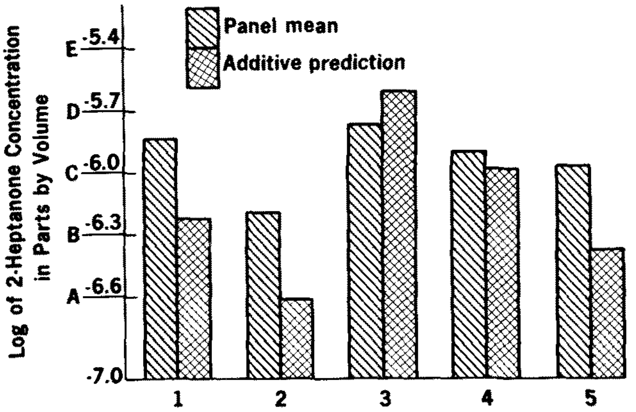

FIG. 7. The observed and calculated flavor intensities of carbonyl mixtures designed to resemble soybean oil oxidized at 55 C. 1 resembles oil oxidized 3 days, 2 is a 6-fold dilution of 1, 3 resembles oil oxidized 5 days, 4 is a 6-fold dilution of 3, 5 is an 80-fold dilution of a mixture resembling oil oxidized 8 days.

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[Received January 1984]