Methional as an Antioxidant for Vegetable Oils[1]

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ABSTRACT AND SUMMARY

Brief heating of safflower oil with 1% by weight of DL-methionine at 200 C stabilized the oil to subsequent autoxidation. Since this treatment also caused development of a strong cabbage-like aroma, it was difficult to follow the oxidation organoleptically. Measurements of oxygen absorption rate and peroxide development confirmed that the heated oil was quite stable. The major product of the reaction between methionine and safflower oil, N(3-methylthiopropyl) linoleic amide, was found to be a prooxidant. There was evidence that methional (β-methylmercaptopropionaldehyde), formed by degradation of methionine, is the active antioxidant. Commercial methional contains significant quantities of a dimer and trimer, both of which were also found to have antioxidant activity. The dimer is a dehydrated aldol condensation product whereas the trimer is cyclic, a substituted trioxymethylene. Methional and its polymers have such strong objectionable odors, even at low concentrations in oil, that their usefulness as antioxidants may be very limited.

INTRODUCTION

The effects of amino acids and proteins on the rate of fat autoxidation have been reported by various investigators (1-3). Amino acids have been mentioned in the literature as antioxidants (4-6) and as components of patented antioxidant mixtures (7-9); but there is still relatively little known about the mechanism of these effects. Koch has suggested that a lipoprotein orientation, possibly induced by processing, may account for the reduced oxidation rate of fat spread as a film on protein (10). Gelatin may exert a protective effect as the result of synergistic action with the tocopherols.

Recently a patent assigned to the Ajinomoto Company of Japan (11) has claimed that small amounts of cystine will stabilize fats, and that this effect is greatly enhanced if the cystine is heated briefly in the fat at 140 C or higher. As a consequence of this claim, a study was begun in our laboratory to determine the effectiveness of various sulfur-containing amino acids.

EXPERIMENTAL PROCEDURES

Materials

Refined safflower oil was obtained from the Pacific Vegetable Oil Co., San Francisco, CA. This oil contained no added antioxidants. DL-methionine and L-cystine were from Nutritional Biochemicals Corp., Rochester, NY. Tertiarybutyl hydroquinone (TBHQ) was furnished by Eastman Chemical Products Inc., Kingsport, TN. Supelcosil-ATF 061 was a product of Supelco, Inc., Bellefonte, PA.

Methods

The rates of oxygen absorption were measured following the method of Bishov and Henick (12) with a modification as described previously (13). Peroxide values were determined by AOCS Official Method Cd 8-53.

Commercial samples of methional were chromatographed using a Perkin-Elmer 900 Gas Chromatograph equipped with a flame ionization detector. The column was 6 ft x 1/8 in. OD stainless steel packed with 10% UC-W98 on 80/100 mesh Anachrom S (Analabs, Inc. North Haven, CT). Helium flow rate was ca. 60 ml/min with a column temperature of 200 C.

Mass spectrometry was carried out with a Consolidated Electrodynamics Corp. 21-110 C mass spectrometer, as described previously (14).

The Varian HA-100 high resolution NMR spectrometer was used to determine structural features of the fractions obtained from commercial methional. Measurements were made on solutions in deuterated chloroform. Lack of deuterium exchange showed the absence of hydroxyl groups. Fraction 2 was analyzed both before and after treatment with Eu $(FOD)_3$. Results are reported in PPM relative to trimethylsilyl (TMS)=0.0 (δ).

RESULTS AND DISCUSSION

In the initial experiments, safflower oil was heated in air for 10 min at 250 C with 1% added L-cystine, with 1% DL-methionine, and with 1% sulfur. All three of the heated samples became dark brown in color and their odors were very unpleasant. Oxygen absorption rates at 60 C are plotted in Figure 1 for the control safflower oil, for a sam-

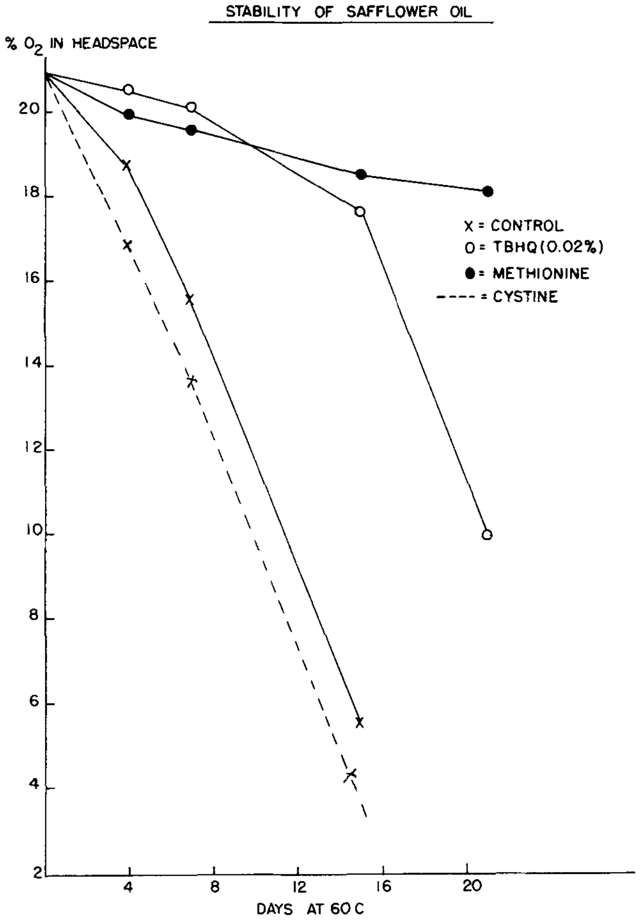

FIG. 1. Oxygen absorption rate of safflower oil heated with methionine.

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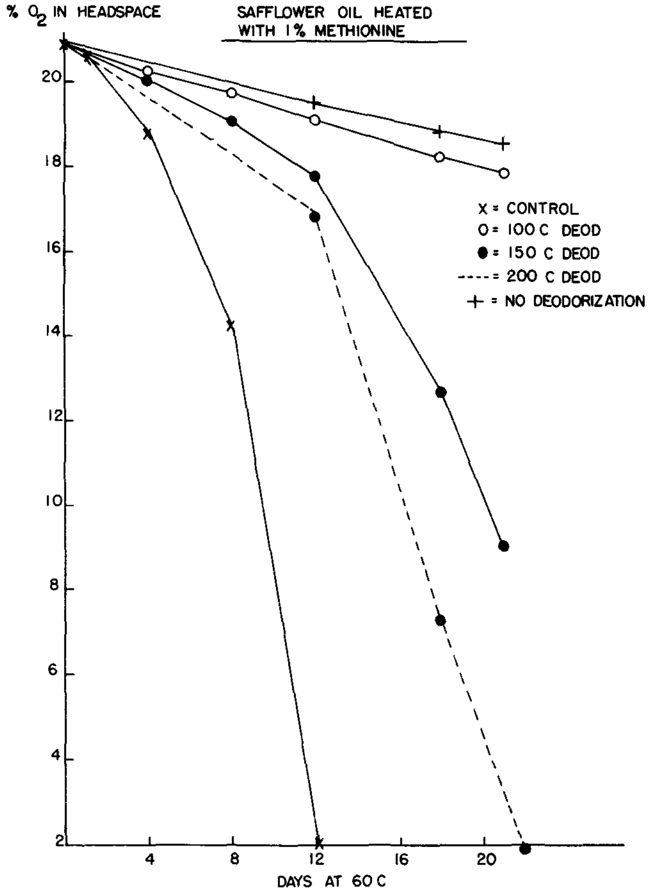

FIG. 2. Effect of deodorization temperature on stability of safflower oil heated with methionine.

ple containing 0.02% added TBHQ, and for those oils heated with cystine and methionine. The control absorbed oxygen rapidly with no evidence of an induction period. Contrary to claims made by the Ajinomoto patent (11) cystine appeared to behave as a pro-oxidant. Methionine, however, exerted a strong antioxidant effect, prolonging the induction period well beyond that observed with TBHQ at the 0.02% level. The curve for the sample containing 1% added sulfur is not shown because it was almost superimposable upon the one for methionine. The rates of hydroperoxide formation at 60 C were also followed on samples of these oils held in loosely capped glass jars in the dark. There was a good correlation between rates of hydroperoxide development and the oxygen absorption data in Figure 1.

When the heating of safflower oil with methionine was carried out under a nitrogen atmosphere, color development was minimized, but the oil still developed a cabbage-like odor. If heating was carried out below 200 C, the methionine did not dissolve completely, and stabilization of the safflower oil was less complete. Attempts were also made to minimize the off-odor development by using smaller amounts of methionine. But stabilization was much poorer as the level was reduced. Even at 0.5% methionine, the safflower oil oxidized much more rapidly than it did after heating with 1% methionine.

Since this 1% level of methionine seemed to be necessary, an attempt was made to eliminate the objectionable odors of the stabilized safflower oil by steam, vacuum stripping. The distillation was carried out in an all-glass laboratory deodorizer for 30 min using a mechanical pump and a dry ice trap. As the stripping temperature was raised from 100 to 150 to 200 C, the oil became progressively more bland, so that after 30 min at 200 C it was virtually odorless. Unfortunately, as the data in Figure 2 illustrate, the effectiveness of the stabilization also becomes less as the result of the higher deodorization temperature. Evidently the antioxidant is either volatile or thermally unstable under these conditions.

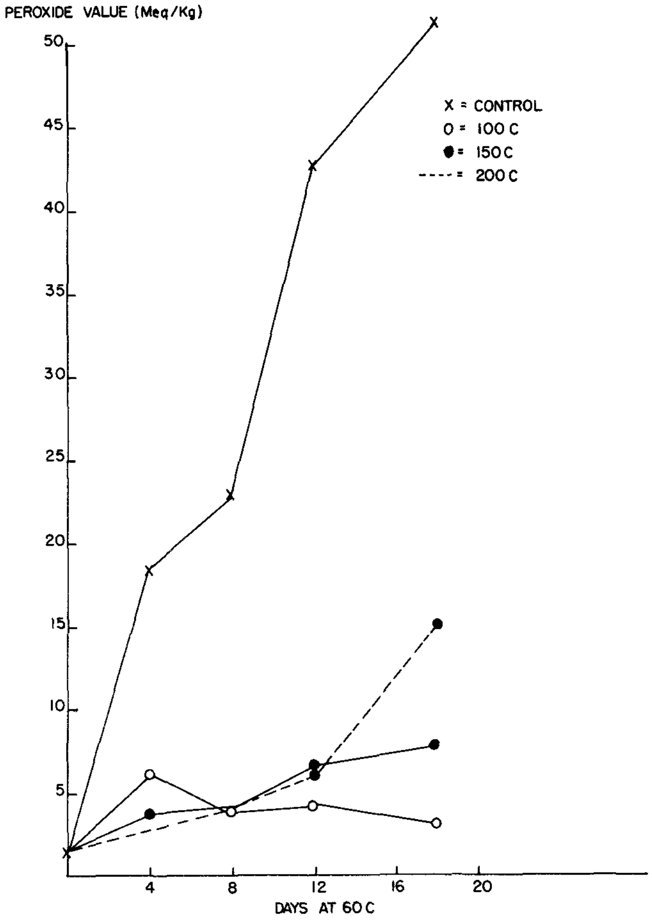

FIG. 3. Peroxide formation in deodorized samples of safflower oil heated with methionine.

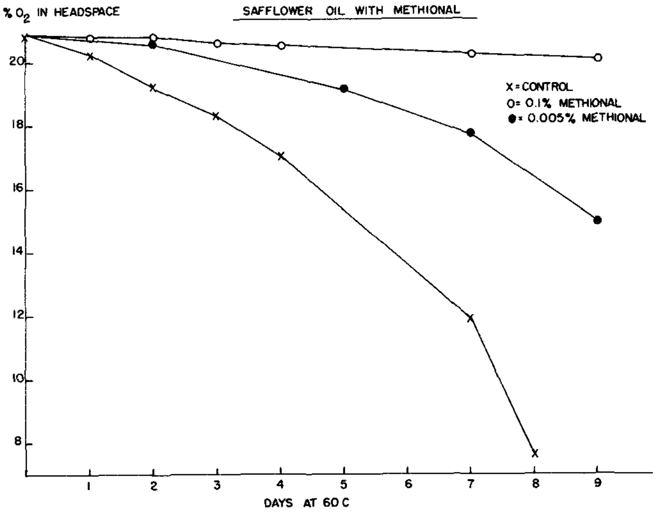

FIG. 4. Stabilization of safflower oil with methional.

In Figure 3 are plotted peroxide values for these same oils during 60 C storage. Both the 150 C and the 200 C samples had absorbed considerable amounts of oxygen after 18-21 days, yet their measured peroxide values in the Schaal oven test were relatively low. Since a drop of 1% in headspace oxygen corresponds to ca. 18 meq/kg of

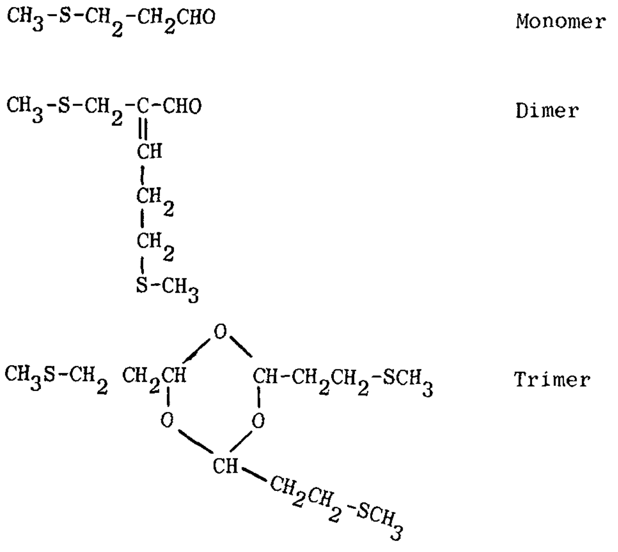

FIG. 5. Structures of fractions from commercial methional.

TABLE I

Nuclear Magnetic Resonance Analysis of Methional Dimer

Peak Position (σ)	Assignment	
9.45	-CHO	-Singlet
6.7	=CH	-Triplet
3.4	$-CH_2-$	-Singlet
2.8	$-CH_2-CH_2-$	-Multiplet
2.15	CH_3-	-Singlet
2.09	CH_3-	-Singlet

absorbed oxygen, the two tests give contradictory indications of stability. Yet the control oil (no methionine) shows a consistent pattern of rapid oxygen absorption and high peroxide values. Evidently the mechanism of the oxidation is altered by the amino acid or its reaction products. This data also suggests that the Ajinomoto patent (11), which relies entirely on peroxide value determinations, may not represent a true picture of the stability attained.

In an earlier publication (15) we reported on the high temperature reactions of fats with amino acids. The major reaction product at 200 C was shown to be an N-substituted amide formed by decarboxylation of the amino acid and displacement of a glyceride ester carbonyl. Even when large amounts of amino acid are heated with fat, the reaction will continue until virtually all the amino acid is consumed, with formation of mono- and diglycerides, and ultimately glycerine. A mixture of 60 parts safflower oil with 40 parts DL-methionine was heated at 200 C for 1 hr, at which time the reaction mixture had become one liquid phase. This mixture was subsequently fractionated by column chromatography on Supelcosil-ATF 061. One of the fractions was shown to be >90% N-(3-methylthiopropyl) linoleic amide. At the 1% level in safflower oil, this amide was found to have a pro-oxidant effect in the oil.

Recently Lee reported on the generation of a potato-like flavor by heating methionine under deep fat frying conditions (16). A group of mercapto aldehydes, including methional (β-methylmercaptopropionaldehyde), was identified. Presumably methional is formed by the Strecker degradation of methionine (17). Perkins has also shown that methionine is degraded in the presence of soy protein, to yield methional under aerobic conditions in boiling water (18). We made several attempts to identify methional in heated mixtures of safflower oil with 1% methionine, but these were all unsuccessful. Nevertheless, the potato cabbage-like odor obtained was certainly characteristic of this compound (19).

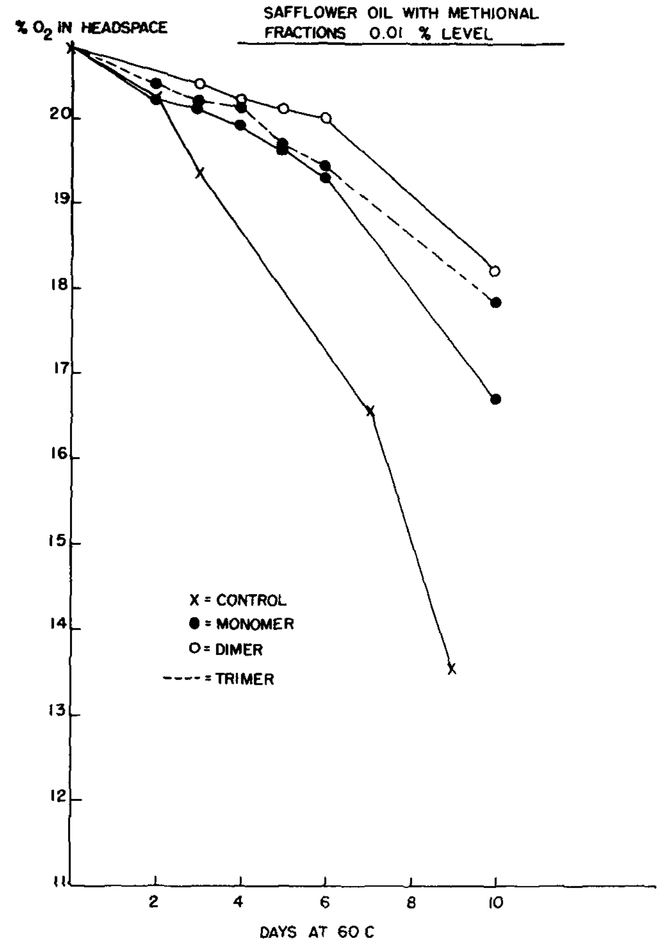

FIG. 6. Stabilization of safflower oil with fractions from commercial methional.

Figures 4 shows rates of oxygen absorption at 60 C with safflower oil containing added commercial methional. Stabilization was quite effective at the 0.1% level, and significant even at 0.005%. Similarly, peroxide values were run during 60 C storage. At the 0.02% level of methional, peroxide accumulation was minimized. Even at the 0.005% leve, there was some degree of protection.

Samples of methional which had been stored for several weeks at room temperature showed changes in character and intensity of odor. Gas liquid chromatography of the material indicated that it was a mixture of at least three components. Subsequent vacuum distillation yielded about 66% of a low-boiling fraction (78-79 C/3 mm), 6% of an intermediate-boiling fraction (114-115 C/0.3 mm) and 28% of a high-boiling pot residue. Gas liquid chromatography of other commercial samples showed different levels of these three fractions, each of which was predominantly one single compound. High resolution nuclear magnetic resonance (NMR) was then used to determine the structural features of these compounds. The low-boiling fraction was found to be monomeric methional (Fig. 5). The intermediate-boiling fraction showed no deuterium exchange and only a small shift after treatment with a Europium complexing reagent. The NMR spectrum (Table I) is indicative of the structure shown in Figure 5, since a hydroxyl peak is ruled out. Mass spectral data confirmed that this was a dehydrated aldol condensation product of methional (mol wt 190).

The high-boiling residue from the distillation was also analyzed by both NMR and mass spectrometry. It was found to be a trimer of methional (mol wt 312) having a cyclic structure (Fig. 5). This is a substituted trioxymethylene and is analagous to paraldehyde, which is formed by the acid-catalyzed polymerication of acetaldehyde.

The three fractions—monomer, dimer, and trimer—were then tested as antioxidants in safflower oil at the 0.01% level. From the oxygen absorption rate data in Figure 6 it is evident that all three are effective antioxidants. These results were confirmed by a Schaal oven test in which hydroperoxide accumulation was also inhibited by each fraction.

It is postulated that methional and its polymers function as antioxidants by conversion of the sulfide linkage to the sulfoxide (20). Unfortunately these materials have such strong odors and flavors, even at very low concentrations, that their usefulness in food products may be very limited.

ACKNOWLEDGMENT

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REFERENCES

1. Bishov, S.J., A.S. Henick, and R.B. Koch, J. Food Sci. 26:196 (1961).
2. Marcuse, R., JAOCS 39:97 (1962).
3. Togashi, H., A.S. Henick, and R.B. Koch, J. Food Sci. 26:186 (1961).
4. Clausen, D.F., W.O. Lundberg, and G.O. Burr, JAOCS 24:403 (1947).
5. Lea, C.H., J. Chem. Ind. 14:107 (1944).
6. Olcott, H.S., and F. Kuta, Nature 183:1812 (1959).
7. Hall, L.A., U.S. Patent 2,518,232 (1950).
8. Lundberg, W.O., U.S. Patent 2.523,127 (1950).
9. Riemenschneider, R., and J. Wundturer, U.S. Patent 2,440,383 (1948).
10. Koch, R.B., in "Symposium on Foods: Lipids and Their Oxidation," Edited by H.W. Schultz, Avi Publishing Co., Inc., Westport, CT, 1962. p. 235.
11. Kawasaki-shi, H.E., U.S. Patent 3,585,223(1971).
12. Bishov, S.J., and A.S. Henick, JAOCS 43:477 (1966).
13. Fioriti, J.A., M.J. Kanuk, and R.J. Sims, Ibid. 51:219 (1974).
14. Fioriti, J.A., M.J. Kanuk, M. George, and R.J. Sims, Lipids 5:71 (1970).
15. Sims, R.J., and J.A. Fioriti, JAOCS 52:144 (1975).
16. S. Lee, "Studies on a Potato Chip-Like Flavored Oil Generated by Deep Fat Frying of Methionine," Rutgers University, 1973 (University Microfilms, Ann Arbor, Mich.)
17. Schonberg, A., and R. Moubacker, Chem. Rev. 50:201 (1952).
18. Shemer, M., and E.G. Perkins, Agr. and Food Chem. 23:201 (1975).
19. S. Arctander, "Perfume and Flavor Chemicals," Vol II, Montclair, NJ, 1969.
20. Barnhard, D., L. Bateman, E.R. Cole, and J.I. Cunneen, Chem. and Ind. (Rev.) 918 (1958).

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