Pro-oxidant Effect of Some Carbonyl Compounds in Vegetable Oils[1]

R. H. ANDERSON and T. E. HUNTLEY[2] James Ford Bell Research Center, General Mills, Inc., Minneapolis Minnesota

Abstract

Certain carbonyl compounds comparable in structure to those which might be produced in browning degradations of sugars were found to act as pro-oxidants in vegetable oils. Action of these compounds as pro-oxidants was apparent in oils held at 57C in open beakers, but not in oils at 99C in the AOM test.

Introduction

THERE HAVE BEEN a number of reports in the literature that antioxidants are formed by browning reactions in heat processed foodstuffs (8,10,16,17,18, 22). The purpose of this paper is to show that under some conditions certain dicarbonyl compounds, comparable in structure with possible intermediates or products of browning reactions, may act as pro-oxidants in vegetable oils.

Several workers (9,11,14,20) have suggested that the mechanism of the browning reaction of sugars with amino compounds involves the formation of ketoseamines resulting from the Amadori rearrangement of the initial aldosylamines. Anet (2) isolated the main product of the reaction of glucose with glycine and showed it to be a ketoseamine. Hodge and Rist (15) postulated a general theory of the mechanism of the browning reaction based on formation of intermediate ketoseamines which subsequently decompose to amino reductones. According to Hodge (12), dehydro reductones are possible precursors of the brown polymers and other complex products resulting from browning reactions of sugars.

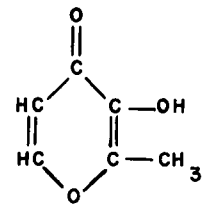
In an investigation of factors responsible for the stabilization of toasted breakfast cereals, Anderson et al. (1) found that potent antioxidants were formed during toasting of cereals, presumably by browning reactions. A host of products results from browning degradations of carbohydrates and an attempt to isolate specific antioxidants from a toasted cereal might be fruitless, or at the least, very difficult. For that reason, Anderson et al. studied effects of specific dehydro reductones and other dicarbonyl compounds added to cereals in the hope that knowledge of the action of these compounds might lead to an understanding of the formation of antioxidants by browning reactions. Results of this study have been reported elsewhere (1); but in a subsequent series of experiments the effects of certain added dehydro reductones and other dicarbonyl compounds on stabilities of vegetable oils were studied.

Experimental

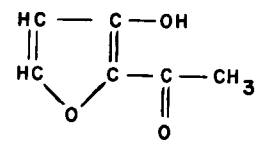
Compounds to be evaluated were each added to unstabilized corn and safflower oils at 50 and 100 ppm. An equal mixture of BHT and BHA at a level of 100 ppm was also added to each oil in order to be sure that the oil would respond to an antioxidant. Fortified and control oils were stored in open beakers in an oven at 57C in an adaptation of the Schall Oven Test. Each sample was run in quadruplicate and each beaker was weighed at intervals in order to obtain a measure of the amt of oxygen absorbed. Peroxide numbers were determined by the Wheeler Iodimetric method on oils in extra beakers. Several samples of control oils were run in each series in order to find the range of variations. In Figure 1 the limits of variation of four samples of the same control oil (averages of four beakers of each) are shown in the two control curves. The oil used was a refined, deodorized corn oil, commerciably available.

Results and Discussion

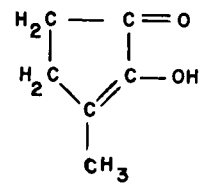
The reductones, ascorbic acid and ascorbyl palmitate, were used for comparison with the dehydro reductones, maltol, kojic acid and kojyl palmitate. Other dicarbonyl compounds comparable in structure to dehydro reductones were used. These compounds included isomaltol, "Cyclotene" and dehydroascorbic acid. Maltol has been found by Backe in baked bread (3) and was isolated by Patton (19) from heated skim milk. Isomaltol was prepared by Hodge and Nelson (13) by heating lactose with a secondary amine. Cyclotene is the trade name of a cyclopentene-ol-one made by the Dow Co., and kojic acid is found in soybean products fermented by Aspergillus molds.



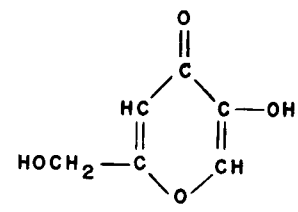
Maltol



Isomaltol



"Cyclotene"



Kojic Acid

Oils containing maltol, isomaltol, Cyclotene and kojyl palmitate absorbed oxygen, developed peroxides and become organoleptically rancid at a more rapid rate than comparable control oils. Oils containing ascorbic acid, ascorbyl palmitate, kojic acid, dehydroascorbic acid and BHT-BHA were more stable to oxidative rancidity than comparable control oils (Fig. 1). Peroxide numbers of oils increased linearly with increasing oxygen absorption. All oils had peroxide numbers over 100 and were organoleptically rancid at a measured oxygen absorption of approx 0.20 g/100 g oil.

Oils used in this study were all refined, deodorized,

[1] Presented at the AOCS Meeting in Minneapolis, 1963. General Mills Central Research Journal Series, Paper No. 353.

[2] Present address, Dept. of Biochemistry, Iowa State University, Ames, Iowa.

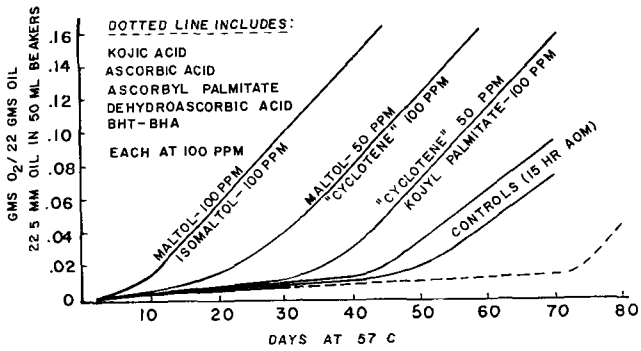


FIG. 1. Rate of gain in wt of oils with time, each in a layer 22.5 mm thick, held in open beakers at 57C. Ratio surface area to wt of oil = 57.

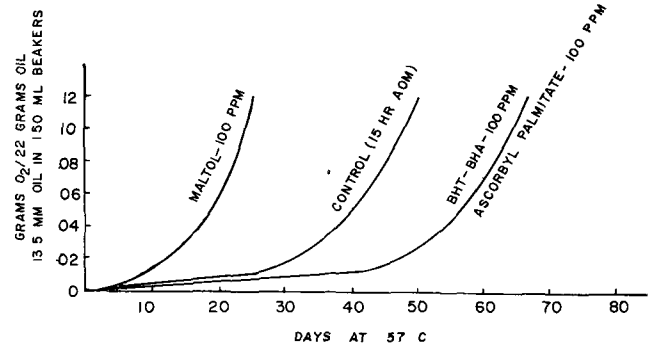


FIG. 2. Rate of gain in wt of oils with time, each in a layer 13.5 mm thick, held in open beakers at 57C. Ratio surface area to wt of oil = 108.

commerciably available corn and safflower oils. In experiments employing different oils the magnitudes of differences between stabilities of oils with and without pro-oxidants and antioxidants varied considerably. However, the generalities previously stated and depicted in Figure 1 held true. Corn and safflower oils of comparable AOM stabilities responded similarly to the inclusion of pro-oxidants or antioxidants. Figure 1 summarizes results of a number of replicate experiments using only one oil, but the relative stabilities of the oil containing the various additives were in the same order as those obtained in experiments utilizing other oils. Curves shown in Figure 1, as well as those in Figures 2 and 3, represent approx averages of values obtained in replicate experiments with a particular oil. The same corn oil was used in experiments summarized by Figures 1 and 2, and a corn oil of lesser stability was used for Figure 3. Behavior of the oils selected was fairly typical of the responses of all oils tested.

Aliquots of the fortified and control oils were run in the AOM test at 99C. The oils containing maltol, isomaltol, Cyclotene and kojyl palmitate had the same AOM stabilities as comparable control oils. The oil containing BHT-BHA, ascorbic acid, ascorbyl palmitate, kojic acid and dehydroascorbic acid had stabilities greater than comparable controls.

Evans et al. (6), in a study of amino reductones as antioxidants, found that the presence of amino reductones in oils caused some error in determinations of peroxide numbers by the Wheeler Iodometric method. The amino reductones were extracted from the fat when water was added to the system and reduced some of the iodine which had been released by the fat peroxides.

To determine if the presence of dehydro reductones caused erroneous peroxide number determinations in our AOM tests, two aliquots of unstabilized corn oil were taken to peroxide numbers of 44 and 108 by bubbling air through the oil heated to 99C. Maltol at a level of 100 ppm was added to the aliquots of the oxidized corn oil and six peroxide number determinations were made on each oil. Values were obtained ranging from 40–43 and from 102–106 on the oils of 44 and 108 peroxide numbers, respectively. A small error may have been introduced by the presence of maltol in the oil, but it had a little effect on the apparent AOM stability of the fortified oil, particularly since all the oils in the AOM test became organoleptically rancid at peroxide numbers of approx 100.

The observation that certain dehydro reductones and other dicarbonyl compounds might act as pro-oxidants in vegetable oils coincides with reports that alpha keto acids [Bhalerao et al. (5)] and certain other carbonyl compounds [Evans et al. (7); and Berry and McKerrigan (4)] may act as pro-oxidants in fats.

Reductones, ascorbic acid and ascorbyl palmitate act as antioxidants in vegetable oils; but the action of kojic and dehydroascorbic acids as antioxidants was not expected in view of the pro-oxidant effects of other dicarbonyl compounds, including kojyl palmitate. Kojic and dehydroascorbic acids are water soluble and were dissolved with difficulty in corn oil only by heating or by prior solution in alcohol. The compounds which acted as pro-oxidants are readily fat soluble as well as water soluble. Work is continuing in order to determine the reasons for the differences in behavior of the compounds tested, but as yet we have no explanation to offer.

Normally in the Schall Oven Test a relatively thin layer of oil is tested for stability. In our studies, increasing the depth of the layer of oil increased the apparent effects of pro-oxidants in that the control oils increased in relative stability more than the oils containing the pro-oxidants. The control oils, as expected, showed greater stability in thicker layers, wherein the rate of oxidation became somewhat limited by the rate of diffusion of air (Fig. 1, 2, 3).

The difference in stability between control oils and those containing pro-oxidants was less pronounced in vegetable oils of relatively lower AOM stability (Fig. 3).

Decreasing differences in stability between oils with and without the added pro-oxidants with more rapid oxidation of the control oil itself in the Schall Oven Test might be predicted from results of the AOM test. Apparently the action of certain dicarbonyl compounds as pro-oxidants is not increased in rate commensurate with an increase in rate of oxidation of the oil itself. In a matter of days in the oven test the effects of the pro-oxidants became manifest, but in the AOM test wherein the oil oxidizes in a few hr the oxidative effects of these compounds were negligi-

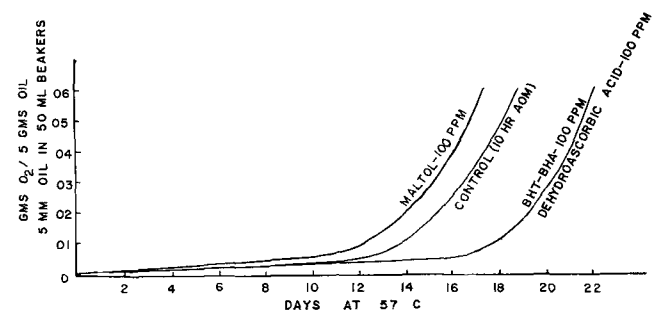


FIG. 3. Rate of gain in wt of oils each in a layer 5 mm thick, held in open beakers at 57C. Ratio surface area to wt of oil = 251.

ble. Presumably, by interpolation, one might expect the effects of certain dicarbonyl compounds as pro-oxidants to be more manifest in a bottled or bulk oil at room temp than in the same oil in a relatively thin layer at 57C.

According to Uri (21), a compound may act as a pro-oxidant if it is converted in any manner to an unstable free radical which can add oxygen to form a peroxide radical which accepts hydrogen from an unsaturated fatty acid to initiate a chain reaction.

It seems odd that the thickness of layers or AOM stabilities of oils had little effect on the time required for those oils to become rancid when the pro-oxidants were added to them. Examination of Figures 1, 2 and 3 shows that control oils decreased considerably in stability in the Schall Oven Test with decreasing layer thickness or AOM stability. However, oils containing a certain pro-oxidant had approx the same measured rate of oxygen absorption. One might expect that dependency of the pro-oxidant action of the dicarbonyl compounds on the presence of oxygen would result in a diminished pro-oxidant effect in thicker layers of oil of higher AOM stability.

We have no suggestions to offer at present to explain mechanisms of pro-oxidant activity encountered, but it was thought worth while to present this paper in order to disclose that certain compounds related in structure to dehydro reductones may act as pro-oxidants in vegetable oils at temp of 57C or less.

ACKNOWLEDGMENTS

Isomaltol, courtesy of J. E. Hodge, No. Utiliz. Res. & Dev. Div., ARS, USDA, Peoria, Ill.

REFERENCES

1. Anderson, R. H., D. H. Moran, T. E. Huntley and J. L. Holahan, Food Technol., in press.
2. Anet, E. F. L. T., Austrialian J. Chem. *10*, 193 (1957).
3. Backe, A., Compt. Rend. *150*, 540 (1910).
4. Berry, N. W., and A. A. McKerrigan, J. Sci. Food Agr. *9*, 693 (1958).
5. Bhalerao, V. R., M. G. Kokatnur and F. A. Kummerow, JAOCS *39*, 28 (1962).
6. Evans, C. D., Helen A. Moser, Patricia M. Cooney and J. E. Hodge, *Ibid.* *35*, 84 (1958).
7. Evans, C. D., E. N. Frankel, Patricia M. Cooney and Helen A. Moser, *Ibid.* *37*, 452 (1960).
8. Findlay, J. D., C. Higginbottom and J. A. B. Smith, J. Dairy Res. *14*, 378 (1946).
9. Gottschalk, A., and S. M. Partridge, Nature *165*, 684 (1950).
10. Griffith, T., and J. A. Johnson, Cereal Chem. *34*, 159 (1957).
11. Hannan, R. H., and C. H. Lea, Biochim. Biophys. Acta *9*, 293 (1952).
12. Hodge, J. E., Agr. Food Chem. *1*, 928 (1953).
13. Hodge, J. E., and E. C. Nelson, Cereal Chem. *38*, 207 (1961).
14. Hodge, J. E., and C. E. Rist, J. Am. Chem. Soc *74*, 316 (1952).
15. Hodge, J. E., and C. E. Rist, *Ibid.* *75*, 316 (1953).
16. Josephson, D. V., and C. D. Dahle, Food Industry *17*, 630 (1945).
17. Lea, C. H., J. D. Findlay and J. A. B. Smith, J. Dairy Res. *14*, 122 (1945).
18. Lips, H. J., JAOCS *28*, 58 (1951).
19. Patton, S., J. Dairy Sci. *33*, 102 (1950).
20. Smith, L. I., and R. H. Anderson, J. Org. Chem. *16*, 963 (1951).
21. Uri, N., "Autoxidation and Antioxidants," ed. W. O. Lundberg, 1st Ed., Vol. 1, John Wiley and Sons, New York, 1961, chapt. 4.
22. Zipser, M. W., and B. M. Watts, Food Technol. *15*, 445 (1961).

[Received December 23, 1963—Accepted May 5, 1964]

Chromatographically Homogeneous Egg Lecithin as Stabilizer of Emulsions for Intravenous Nutrition[1, 2]

H. J. ZERINGUE, M. L. BROWN and W. S. SINGLETON, Southern Regional Research Laboratory,[3] New Orleans, Louisiana

Abstract

Physically stable emulsions of cottonseed and soybean oils at 20% concn were prepared with chromatographically homogeneous egg lecithin at 1% concn as the sole emulsifier, and a 2.5% solution of glycerol as the aqueous phase. The physical stability of the emulsions was a function of the pH of the product, optimum pH 6.6–6.8. Aqueous solutions of dextrose and sorbitol decreased in pH to 4.8 when autoclaved, regardless of prior adjustment of pH to as high as 8.5, and emulsions in which these solutions were used as the aqueous phase exhibited phase separation. There was no significant decrease in pH, and no phase separation, in emulsions which contained glycerol solution as the aqueous phase. It appears that glycerol is superior to dextrose as the isotonic agent in lecithin-stabilized emulsions for intravenous nutrition.

Particle sizes and their distribution in lecithin-stabilized emulsions of cottonseed and soybean oils were determined by means of a Coulter Counter. Approximately 99% of the oil in these emulsions was dispersed as particles whose diameters were no larger than 5 μ.

Introduction

FAT EMULSIONS for intravenous nutrition have been widely proposed, as may be noted in the extensive review by Geyer (3). The emulsifying systems of many of these proposed emulsions include phosphatides, the majority of which are soya phosphatides, although egg phosphatides also have received attention. Schuberth and Wretlind (5) described the use of egg phosphatides as the emulsifier for a soybean oil emulsion and present physiological results which they obtained; however, the phosphatides used were impure, since the analytical results given are not theoretical for phosphatidylcholine. In an investigation of highly purified egg phosphatides, principally lecithin, as the major component of an emulsifier system for the preparation of fat emulsions, Yeadon et al. (9) concluded that purified egg lecithin was not an efficient emulsifier, particularly with respect to autoclaving stability. These workers found that certain additives to the lecithin emulsifier system enhanced its effectiveness, but do not give any explanation for this effect.

Phospholipids are naturally occurring components of body fluids and tissues, and therefore it seems very reasonable to use a pure natural lecithin as the emulsifier for intravenous fat emulsions. Recently, a rapid method for purifying egg phosphatides by column chromatography has been published by this Laboratory (7), and chromatographically homogeneous lecithin has been investigated as the sole emulsifier in fat emulsions. This report presents the results of that investigation. It should be clearly understood that the described emulsion at this time is intended only for experimental use in animals. Such tests are underway at other institutions.

[1] Presented at the AOCS Meeting, New Orleans, 1964.
[2] Supported by funds from the Office of the Surgeon General, U.S. Army, Washington, D.C.
[3] A laboratory of the So. Utiliz. Res. & Dev. Div., ARS, USDA.