Addition of Hydrogenated Fats to Chocolate to Improve Heat Resistance[1,2]

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CHOCOLATE contains about 30% by weight of cocoa fat. This fat, also known as cocoa butter, consists of two glycerides, 2-oleopalmitostearin and 2-oleodistearin, about 57 and 22% by weight, respectively (1, 3). The unusual composition of cocoa fat imparts to chocolate unique properties. Chocolate is quite hard and brittle at room temperatures below about 78°F.(25.6°C.); yet, when eaten, it melts in the mouth quickly and completely, producing a pleasing sensation.

Unfortunately at summer temperatures above about 82°F.(27.8°C.) chocolate bars become soft and will not retain their shape; fat leakage tends to occur. Because of this physical instability at summer temperatures, confectioners in the United States curtail chocolate production during the summer months.

Chocolate-type confections, which contain hard fats in addition to cocoa fat, are produced during summer as well as other seasons of the year. The hard fats added in such confections are mainly partially hydrogenated domestic oils or imported lauric acid-type oils or mixtures of these. Almost invariably the hard fats which are added are composed of numerous types of glycerides which differ in fatty acid composition and configuration from those found in cocoa fat. Such added fat mixtures frequently will soften and melt over a relatively wide temperature range. Also such fat mixtures will increase the melting and softening range of the cocoa fat in chocolate-type confections. Thus the use of a partially hydrogenated oil or a lauric acid-type oil is not the ideal solution to improving the physical properties of chocolate.

A reasonably good solution to the problem would be the incorporation in the chocolate of a minor amount of some material which would not impair the eating quality yet would give rigidity to the mass and retard fat leakage should the ambient temperature exceed the softening point of the cocoa fat.

To find a suitable additive, numerous compounds and products were tested. Included were dextrins, starch, natural gums, protein preparations, fatty acids, fatty acid esters of sugars, different glycerides, emulsifiers, and various combinations of these. Of the compounds and products tested completely hydrogenated cottonseed oil, completely hydrogenated cocoa butter, and similar fats performed best.[4]

Completely hydrogenated cottonseed oil was found to be particularly well suited in a number of respects.

When completely hydrogenated cottonseed oil crystallizes in liquid cocoa butter, the crystals are minute and probably some are submicroscopic in size. At ordinary rates of formation the crystals remain suspended in the liquid oil, and at a solids content of 10–12% a shortening-like consistency is attained.

The completely hydrogenated cottonseed oil, melting point above 61°C.(142°F.), is quite insoluble in cocoa butter at the melting point of the latter, which is 33–35°C.(91–95°F.). While the exact solubility was not determined, it is undoubtedly almost identical with that of completely hydrogenated cottonseed oil in cottonseed oil as shown in Figure 1 (4). The solubility of a hard fat in a liquid oil is relatively independent of the nature of the liquid oil.
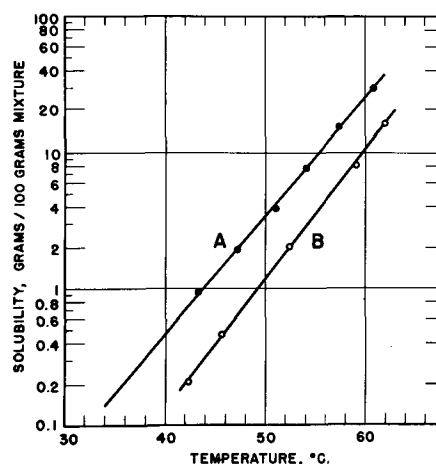

FIG. 1. Solubility of (A) hydrogenated cottonseed oil (iodine value 1.1) in cottonseed oil and (B) tristearin in triolein.

The presence in completely hydrogenated cottonseed oil of essentially only a few triglycerides, tristearin, and some palmitostearins is a contributing factor in the low solubility observed. However the major factor is the nature of the triglycerides. The completely hydrogenated cottonseed oil is soluble in cocoa butter at 35°C.(95°F.) only to the extent of a fraction of 1%. Such a solubility is in this case apparently too low for the dissolved fat to interfere significantly with the softening range and melting characteristics of the cocoa fat in chocolate. Also this slight solubility does not interfere significantly with the seeding, solidification, and tempering of the cocoa fat in the manufacture of chocolate.

On the basis of the considerations just mentioned, it is apparent that the addition of a relatively small quantity of completely hydrogenated oil to chocolate will improve heat resistance. This technique might even be used to improve the heat resistance of chocolate-type confections. The object of the present study was to ascertain to what degree the addition of hard fat improves heat resistance and affects other important properties of chocolate.

[4] For the purpose of this discussion the term "completely hydrogenated" will refer to oils hydrogenated to an iodine value of about 1 and below, a level which can be reached without unduly prolonging the hydrogenation reaction.

TABLE I
Composition of Chocolate and Chocolate-Type Bars Evaluated by Taste Panel

Sample No.	Composition,[a] wt. %							
	Sugar	Nonfat milk solids	Milk solids, whole	Chocolate liquor	Cocoa butter	Completely hydrogenated cottonseed oil	Emulsifier [b]	Water
1	42.3	15.5	0.0	(17.0)[c]	(23.4)[d]	1.34	0.5	0.0
2	42.3	15.5	0.0	(17.0)[c]	(23.4)[e]	(1.34)[f]	0.5	0.0
3	44.1	16.2	0.0	17.1	19.1	(3.0)[f]	0.6	0.0
4	49.7	9.0	3.8	10.4	27.1	0.0	0.0	0.0
5	47.1	8.7	3.7	10.1	26.5	3.1	0.0	0.0
6	47.6	8.7	3.8	10.0	26.2	3.1	0.63	0.0
7	47.3	8.6	3.8	9.9	26.2	3.1	0.62	0.8
8	47.6	8.7	3.8	10.0	26.3	3.1	0.00	0.8

[a] Salt and vanillin added to Samples 1–3 to obtain good flavor. Sample 4 was a commercial sweet milk chocolate, coating type, containing vanillin and artificial flavoring. Samples 5–8 obtained by additions to Sample 4.
[b] A fatty acid ester of polyglycerol.
[c] Cocoa powder (15% fat) substituted in indicated quantity for chocolate liquor.
[d] Commercial candy fat, m.p. 118.8°F.(48.2°C.), used in quantity shown.
[e] Commercial candy fat, m.p. 95.5°F.(35.3°C.), used in quantity shown.
[f] Completely hydrogenated cocoa butter used in quantities shown.

Eating Quality and Appearance

Poor mouthing quality is one objectionable result of incorporating a substantial quantity of high-melting fat in chocolate-type confections. Its manifestation is a waxy feel in the mouth and an apparent lack of melting when the confection is eaten. To determine at what level poor mouthing quality appears when a completely hydrogenated oil is added to chocolate, a series of tests was made with a chocolate of the following weight composition: sugar, sucrose 45.7%; nonfat milk solids 16.9%; cocoa butter 19.7%; and chocolate liquor 17.7%. Chocolate liquor, the roasted and ground meats of cocoa beans, contains about 54% fat by weight. Hence the total amount of cocoa fat in the above formulation was about 29%.

Amounts of completely hydrogenated cottonseed oil ranging from 2–20%, based on the weight of cocoa fat, were mixed into the chocolate at a temperature just above 60°C. While mixing was continued, the mass was cooled. Just before becoming too stiff to be molded, the mass was seeded with a small amount of cocoa butter; the quantity used was included in the formula given above. The molded bars were cooled in the refrigerator for 1 hr. at about 5°C.(41°F.) and then were tempered further by storing them overnight at room temperature (about 26°C. or 79°F.).

Those chocolate bars containing about 10% or less of completely hydrogenated cottonseed oil, based on the total weight of cocoa fat, had a good mouthing quality. At a 5% level the mouthing quality was practically indistinguishable from that of a control containing no hydrogenated cottonseed oil. At a 15% level waxiness was definitely present while at a 20% level it was quite marked.

The appearance of the bars was generally good. The gloss was about the same as that of the control.

Tests were made to determine whether or not the temperature at which the bars were molded had a significant effect on the mouthing quality. Increasing the molding temperature up to 60°C.(140°F.) produced no adverse effect on this property. Decreasing the temperature below that normally used produced bars of a grainy structure but did not increase the degree of waxiness.

The degree of waxiness could definitely be decreased by addition to the chocolate of a small amount of emulsifier, 1–2% on a total fat basis. Several types of emulsifiers were effective, including soybean lecithin and a fatty acid ester of polyglycerol (Drumulse 536 R, E. F. Drew Company).[5] Emulsifiers also have

the desirable effect of reducing the viscosity of melted chocolate (5).

The mouthing quality of chocolate containing completely hydrogenated cottonseed oil and an emulsifier could be improved even more by the addition of about 2.5% water, based on the total weight of fat. However the addition of water markedly increased the viscosity of the melted chocolate. Also chocolate bars containing moisture tended to have a grainy structure and to develop sugar bloom on temperature cycling.

The results obtained with completely hydrogenated cottonseed oil were duplicated by using other similar fats, including tripalmitin, tristearin, completely hydrogenated soybean oil, and completely hydrogenated cocoa butter.

To evaluate further the several factors involved in fortifying chocolate and chocolate-type confections, a series of samples having the composition shown in Table I was prepared. In all instances the ingredients were heated to just above 60°C.(140°F.) and well mixed. The seeding, molding, and tempering procedure mentioned above was followed. Sample 4, the control, was a sweet milk chocolate, commercial coating type. Samples 5–8 were obtained by adding various combinations of hard fat, emulsifier, and water to the sweet milk chocolate. The samples were tested at the Quartermaster Food and Container Institute. The results obtained are recorded in Table II.

The taste panel at the Institute gave the sweet milk chocolate an acceptance rating of 7.3, based on a 9-point quality scale. Samples 3, 5, and 6 were given numerical ratings, which indicated they were very good. According to the panel the use of emulsifier and water in the formulations did not improve the quality.

As an aid in interpreting the acceptance data, it should be mentioned that none of the panel members were trained in either candy or fat technology. In the evaluation there may have been a tendency to associate flavor and mouthing quality, and probably mouthing quality involves other factors than the degree of waxiness.

Holding the samples for 72 hrs. at 100°F.(37.8°C.) was a severe test. At this temperature the cocoa fat melted completely; and bloom, which can be associated with slow solidification in the absence of proper seed crystals, should be expected. Confections intended for civilian use usually are not subjected to a temperature of 100°F.

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[5] It is not the policy of the Department to recommend or endorse the products of one company over similar products manufactured by others.

Hardness

Hardness determinations (Table II) are only approximately quantitative and to an appreciable degree are determinations of the viscosity or consistency of the mass. The true hardness of chocolate at temperatures below about 24°C.(75°F.), where the mass contains over 90% of solids, is also an important factor in acceptability.

To establish the effect on hardness of adding a small amount of high melting fat to chocolate, a series of samples was prepared in which completely hydrogenated cottonseed oil was added to sweet milk chocolate, coating type, at levels of 3, 7, and 10%, based on the weight of cocoa fat. The sweet milk chocolate used was the same as that listed as Sample 4, Table II. The several samples, including a control consisting of the sweet milk chocolate alone, were seeded, solidified, and tempered in the usual manner. Special care was taken to give all four samples exactly the same thermal treatment.

Hardness indices were determined by a modification of the Brinell hardness test for metals (2). In this modified test a steel ball was pressed into the molded surface of the bar with a force sufficient to make only a slight impression, sometimes barely visible to the eye. The hardness index in terms of kilograms per square centimeter was calculated from the area of the impression and the force used. The data obtained with the four bars are recorded in Figure 2.

The incorporation in the chocolate of the completely hydrogenated cottonseed oil increased the hardness by very moderate amounts. At all except one test temperature the experimentally determined hardness indices increased as the proportion of hard fat increased.

In other hardness tests it was found that the addition of about 0.3% lecithin, fat basis, to a formulation containing 10% of completely hydrogenated fat, cocoa fat basis, lowers the hardness index about 25% at room temperature. Molding temperature also affects the hardness of a chocolate bar containing completely hydrogenated oil. Increasing the molding temperature from 35 to 60°C.(95 to 140°F.) can increase the hardness by about 80% at room temperature of a bar containing 10% of completely hydrogenated oil, calculated on a cocoa fat basis.

Consistency

To determine quantitatively the consistency of fortified chocolate at a temperature above the melting point of cocoa fat, the four samples represented in Figure 2 were tested by the cone penetration method after various periods of time at 36°C.(96.8°F.). Also tested was a sample similar to Sample D except that
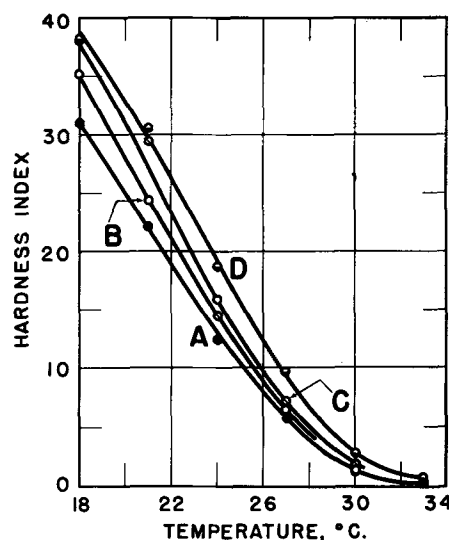

FIG. 2. Hardness vs. temperature curves for (A) sweet milk chocolate, coating type, and (B, C, and D) the same milk chocolate after addition of 3, 7, and 10%, respectively, of completely hydrogenated cottonseed oil, additions calculated on the basis of total cocoa fat.

it contained 0.3% soybean lecithin, calculated on a cocoa fat basis.

The cone penetrometer and technique used were those specified in Method D 217-48 of the American Society for Testing Materials except that the weight of the cone and movable attachments was 50 g. instead of 150 g. The test results are recorded in Table III. By way of comparison, the cone penetration value for margarine and dairy butter at room temperature is about 160. Obviously chocolate can be made quite firm at 36°C.(96.8°F.) by the addition of a limited amount of completely hydrogenated oil. Based on the total weight of the chocolate, this amount need not be over 3%. The simultaneous addition of a small amount of lecithin, 0.1% based on the weight of the chocolate, counteracts to a small degree the effect of the addition of the hydrogenated fat.

While the fortifying of chocolate increases its stiffness and hence performance at summer temperatures of about 36°C.(96.8°F.), there are certain attendant disadvantages. In the manufacture of bars the mass becomes so viscous at the solidification point of the cocoa fat that proper seeding of the latter becomes difficult. However it was found that the cocoa fat could be tempered without prior seeding by cooling the chocolate mass rapidly to about 5°C.(41°F.), then heating it rapidly to about 31°C.(88°F.), and finally cooling it to room temperaturee. Such a treatment apparently did not produce much bloom.

TABLE II
Taste Panel Evaluation and Other Performance Data for Chocolate and Chocolate-Type Bars

Property	Formulation No.							
	1	2	3	4	5	6	7	8
Taste panel rating [a]								
Flavor	5.5	6.6	6.8	7.3	7.1	6.9	5.8	6.1
Mouthing quality	5.0	6.1	7.1	7.3	7.1	7.0	6.0	5.3
Hardness after 72 hrs. at 100°F. (37.8°C.) [b]	Hard	Hard	Fairly hard	Very soft	Moderately soft	Fairly hard	Fairly hard	Fairly hard
Fat leakage during 72 hrs. at 100°F. (37.8°C.) [c]	None	None	Slight	Heavy	Moderate	Slight	Slight	None
Bloom on cooling to room temperature after 72 hrs at 100°F.(37.8°C.)	None	None	Heavy	Heavy	Heavy	Moderate	Slight	None

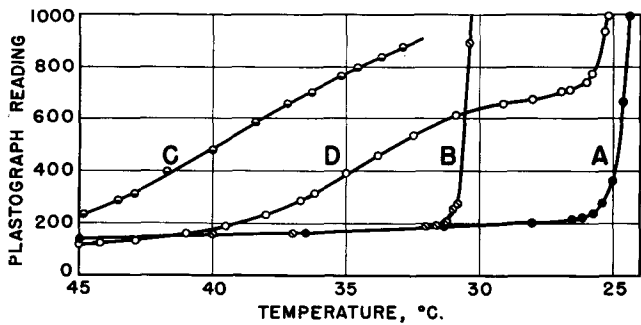[a] Based on a 9-point quality scale.   [b] Judged by touch.   [c] Judged by leakage through folds of wrapper.

FIG. 3. Consistency changes obtained on cooling while simultaneously working chocolate and modified chocolate: (A) commercial, sweet milk chocolate, coating type, cooling rate 1°/2 min.; (B) the same chocolate, cooling rate 1°/60 min. below 32°C.; (C) the same chocolate with 10% of completely hydrogenated cottonseed oil, cocoa fat basis, added, cooling rate 1°/5 min.; and (D) the same chocolate with 10% completely hydrogenated cottonseed oil and 2% emulsifier, Drumulse 536 R, calculated on a cocoa fat basis, added, cooling rate 1°/2 min.

Use of fortified chocolate for coating and enrobing presents more difficult problems. The viscosity, even above the melting point of the cocoa fat, is so high that the application of thin coatings is impossible with commercial enrobing machines.

The viscosity-temperature data obtained on cooling sweet milk chocolate of the coating type, the same product represented in Figure 2 and Table III, and this product after fortification are presented in Figure 3. The data were obtained with Plastograph (Brabender Corporation), a machine which records the force required to mix or knead a plastic mass at a constant rate and at controlled temperatures.

TABLE III

Effect of Addition of Completely Hydrogenated Cottonseed Oil on Consistency of Milk Chocolate

Sample [a]	Amount of hydrogenated oil [b]	Consistency, cone penetration, mm./10, on storage at 36°C. (96.8°F.)		
		4 hrs.	6 hrs.	72 hrs.
A	0.0	>216	....	....
B	3.0	163	168	160
C	7.0	71	65	77
D	10.0	51	51	45
E [c]	10.0	61	62	54

[a] Samples A–D are same as those represented in Figure 2.
[b] Calculated on basis of cocoa fat.
[c] Same as Sample D, except 0.3% lecithin, fat basis, added.

The viscosity-temperature curves in Figure 3 were obtained after holding the temperature at 45°C. (113°F.) until the viscosities reached a constant minimum value.

As an aid in orientation a Plastograph reading of 1,000 corresponds to a viscosity of about 50,000 centipoises. A commercial shortening at 27°C.(81°F.) will give a Plastograph reading of about 100 after mixing for 15 min. though the reading when the mixing is started may be as high as 400.

In interpreting the curves it is obvious, of course, that the nearly vertical segments of curves A, B, and D represent regions of rapid crystallization of cocoa fat. The viscosity of the mixture represented by curve C practically reached the upper limit of the chart without any cocoa fat crystallizing. The uniform increase in viscosity with a decrease in temperature apparently was solely a function of the amount of hard fat crystallizing out of solution.

Fat Leakage

Because there is no generally recognized test for quantitatively measuring the rate of fat leakage for products like chocolate, shortening, and margarine, several logical test procedures were devised and evaluated. The one giving the most reproducible results was carried out as follows. A strip of No. 2 Whatman filter paper measuring 0.4 × 4.0 cm. was placed on a 1 × 3 in. microscope slide, to the underside of which had been taped a section of 1-mm. graph paper so that distances along the strip of filter paper could be measured directly. A 0.5-cm. cube of the chocolate sample, whose rate of fat leakage was to be tested, was placed on one end of the strip of filter paper, and the remaining 3.5-cm. length of filter paper was covered with a second glass slide. The entire assembly was placed in a constant temperature cabinet equipped with a glass door and maintained at the desired test temperature. Fat leakage in millimeters was recorded at regular time-intervals. To ensure obtaining the best possible results, samples of the same series were run simultaneously by using strips of filter paper cut from the same sheet.

Data obtained in one typical series of samples tempered in exactly the same manner are given in Figure 4. These data indicate that the rate of fat leakage is reduced by the addition of completely hydrogenated oil to a chocolate formulation, the presence of emulsifier has no appreciable effect on the rate, and the molding temperature does affect the rate. On the basis of other data it also was found that the manner of solidification and degree of tempering of a chocolate sample influences the rate of fat leakage.
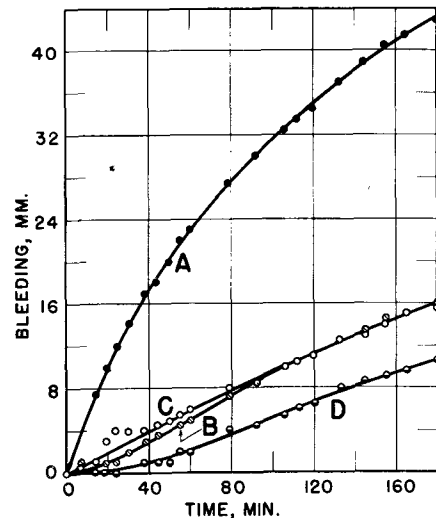

FIG. 4. Fat leakage rate at 36°C.(96.8°F.) for (A) commercial, sweet milk chocolate, coating type; (B) the same chocolate with 10% completely hydrogenated cottonseed oil, cocoa fat basis, added; (C) the same chocolate with 10% completely hydrogenated cottonseed oil and 1.1% lecithin, calculated on a cocoa fat basis, added; and (D) formulation B molded at 60°C.(140°F.) instead of 35°C.(95°F.).

Summary

An investigation was made of the possibility of fortifying chocolate better to withstand summer temperatures by adding relatively small proportions of completely hydrogenated cottonseed oil and similar products.

Proportions of hydrogenated oils up to 10%, based

on the weight of cocoa fat, do not affect mouthing quality significantly, yet they impart marked rigidity to the chocolate mass at temperatures at which cocoa fat softens and melts. Because the hard fat is practically insoluble in cocoa fat at the melting point of the latter, the hard fat, under the conditions adopted, does not alter the melting characteristics of the cocoa fat, and the short softening range of the cocoa fat is retained.

The addition of the completely hydrogenated oil greatly retards the rate of fat leakage from chocolate at temperatures of about 36°C.(97°F.).

The addition of small amounts of very hard fats to chocolate should be useful in improving the performance of molded bars. However if the modified chocolate is to be used for coating confections, the increase in viscosity which results on the addition of the hard fat presents a serious disadvantage.

REFERENCES

1. Chapman, D., Crossley, A., and Davies, A. C., J. Chem. Soc., 1957, 1502–1509.
2. Lovegren, N. V., Guice, Wilma A., and Feuge, R. O., J. Am. Oil Chemists' Soc., 35, 327–331 (1958).
3. Meara, M. L., J. Chem. Soc., 1949, 2154–2157.
4. Ward, T. L., Gros, Audrey T., and Feuge, R. O., J. Am. Oil Chemists' Soc., 32, 316–318 (1955).
5. Working, E. B., U. S. Patent 1,781,672 (November 11, 1930).

Rate Studies of Unsaturated Fatty Acid Oxidation Catalyzed by Hematin Compounds[1]

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HEMATIN catalyzed unsaturated fatty acid oxidation is a basic mechanism of in vivo pathological reactions found in vitamin E-deficient animals (7, 14) and in oxidative fat rancidity of meat, poultry, and fish (11, 12, 16). In contrast to these deleterious reactions, hematin catalysis might be used beneficially. Hematin catalyzed peroxide decomposition might be used in processes requiring initiation of free-radical propagated polymerization reactions.

Many important aspects of this catalytic oxidation are still unknown. The catalytic activity of the hematin compounds depends on the presence of peroxide in the system (13), but little is known concerning the interdependence of catalyst, unsaturated fat, and peroxide concentrations and their effect on the rate of the oxidative reaction. The catalysis has been reported to occur only in heterogeneous systems (5, 11), but no systematic study of this phenomenon has been conducted. Long, unexplained induction periods have also been observed (1, 13). In order to help clarify these problems and to establish a firmer basis for further work, a comprehensive study was carried out in which the effects of homogeneous and heterogeneous linoleate, hydroperoxide concentration, catalyst concentration, and temperature on the rate of oxygen absorption were determined.

The rate of oxygen absorption is a good measure of the rate of oxidation of unsaturated fatty acid and thus of the over-all reaction, but it yields very little information concerning the initiation reactions. The kinetics of this important reaction between hematin compound and fatty acid hydroperoxide have never been studied, nor have the peroxidative activities of the various hemoproteins and related compounds been directly determined. In order to study this reaction a spectrophotometric method was developed, based on the decrease in diene conjugation of linoleate hydroperoxide when catalytically decomposed by hemoglobin. Using this technique, a study was made of the effects of linoleate hydroperoxide concentration, hemoglobin concentration, and temperature on the rate of the reaction. In addition, the catalytic activities of several hemoproteins, metallo-protoporphyrins, and other interesting metal-chelate compounds were determined.

Experimental

Reactants. Homogeneous (soluble) linoleate was prepared from potassium linoleate by dilution with 0.1 M ammonium buffer, pH 9, and heterogeneous (colloidal) linoleate by dilution with 0.1 M phosphate buffer, pH 7 (11, 13). Linoleate hydroperoxide was prepared by the lipoxidase catalyzed oxidation of potassium linoleate (9). Purified hemoglobin was prepared from fresh cattle blood.

Measurement of Oxygen Absorption. Standard manometric techniques, employing a Warburg respirometer, were used to follow the rate of oxygen absorption. With the exception of the study to determine the effect of temperature on the rate of the reaction, in which the flasks were gassed with oxygen, air was used as the gas in all experiments. The rate of oxidation was obtained from the slope of the initial straight line portion of the oxygen absorption versus time plots. When induction periods were encountered the rates were those after the induction period.

Reaction Systems for Unsaturated Fatty Acid Oxidation. A comparison of the rates of oxidation of homogeneous and heterogeneous linoleate in the presence of 7.5×10^{-5} M hemoglobin was made at various linoleate concentrations. The ability of hematin to catalyze the oxidation of homogeneous linoleate was also tested, and similar results were obtained.

To determine which of the components were responsible for the occurrence of induction periods in the more dilute solutions, the following series of experiments were carried out: a) total linoleate and linoleate hydroperoxide varied, hemoglobin constant; b) linoleate hydroperoxide varied, total linoleate and hemoglobin constant; c) hemoglobin varied, total linoleate and linoleate hydroperoxide constant.