or flavin-type of coenzyme. All these other oxidoreduction systems are two electron-transfer systems. Lipoxidase catalysis involves only the momentary transfer of one electron. This clearly emphasizes the essential difference between the two types of catalysis.

According to Leach (12), the role of thiol groups in the protein moiety may be two-fold; as one electron system mediating between pairs of bivalent redox systems and as the initiator of reaction chains. In lipoxidase catalysis however there is no need for mediation since the nature of oxidation is univalent itself. Hence the purpose of thiol groups in urd-bean lipoxidase may be the initiation of reaction chains. The theoretical basis for this surmise is afforded by the papers of Waters and associates (7, 15, 28), Leach (12), and Barron and associates (1, 2). Bickel and Kooyman (4) have pointed out that these reactions should have low-activation energy and may be reversible at room temperature. The existence of thiol radicals has been repeatedly demonstrated (1, 13, 14).

In the light of the above the first step in the catalysis of linoleate oxidation could be represented as follows:

$$-CH=CH-CH_2-CH=CH-+\cdot SR-Lipox \rightleftarrows$$
$$-CH=CH-\dot{C}H-CH=CH-+HSR-Lipox$$

This reaction depicts the essential thiol radical initiating the lipoxidase reaction. The remaining sequence of steps in the oxidation could be exactly the same as depicted in Figures 2-B and 2-C, which is fully discussed in the previous section.

Summary

The comparative properties of lipoxidases from urd beans, mung beans, wheat, and peanuts have been determined and discussed. Evidence has been presented to suggest the participation of essential thiol groups in urd-bean and mung-bean lipoxidase catalysis but not in soybean, wheat, pea, and peanut lipoxidase catalysis. This suggests the possible occurrence of two types of lipoxidases in nature.

On the basis of these and other available experimental results, mechanisms for lipoxidase catalysis are proposed.

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The Composition of Bloom Fat in Chocolate

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THE FORMATION of a white film on the surface of chocolate, whether in the form of molded bars or coatings for centers, has plagued the industry since the use of chocolate began. Since this discoloration is supposed to resemble the bloom on grapes, it is known as "bloom." There are two distinct blooms which occur on chocolate, "fat bloom," so called because it is composed largely of fat, and "sugar bloom," composed mainly of sugar crystals. It is with "fat bloom" that we will deal here, and we shall call it simply bloom.

There has not been a great deal published on the actual composition of bloom. Whymper was the pioneer in the field of studying fat bloom on chocolate (16, 17). Sachsse (14, 15) described the different types of fat bloom. He found that the fat located in streaks below the surface of the chocolate had a melting point of 30°C. The fat which had appeared as bloom on the surface of well-tempered chocolate after six months had a melting point of 34°C. and, on chocolates which had been stored for several years, had the appearance of feathers and melted at 36°C. These melting points confirm unpublished findings of one of the authors (5). Neville *et al.* (12) found the iodine number of the surface layer of fat on a slab of cocoa butter to be lower than that of cocoa butter. Several investigators studied the effect of various centers upon the fat blooming of chocolate coatings (2, 5, 7, 14). Whymper (17) and Fincke (6) studied the effect of oil from covered nutmeats.

Harris and Shillaber (8) as well as Hettich (9) studied fat bloom by observing the surface of blooming chocolate under a microscope and noticed tiny beads of oil coming to the surface and then crystallizing, after which the typical white discoloration formed on the surface. From this and other observations Fincke (6) and others (9, 10, 11, 14) state that fat bloom is a physical phenomenon, that is, when an unstable, polymorphic modification of the fat

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changes to a more stable one and latent heat is evolved, some parts of the melted fats are forced out and recrystallized on the surface of the chocolate as "fat bloom."

Some investigators (12, 16, 17) state that fat bloom is caused by the separation and crystallization of the higher melting fraction of the cocoa butter. The melting point of bloom fat is 1–4°C. higher than the melting point of regular cocoa butter (17). Altogether there seem to be a number of causes for the appearance of bloom. In any case it is evident that some change in internal stresses forces out minute globules of fat. The causes of this stress may be chemical, physical, electrical, or any combination of these.

At this point it might be well to mention one form of bloom which, while different in nature, is significant. This bloom occurs when other hardened vegetable fats are added to chocolate to replace part of the cocoa butter. When these vegetable fats are added to the chocolate in certain proportions, fat bloom will always occur and this bloom can be wiped off easily. By subjecting this bloomed chocolate to just sufficient heat to cause the bloom to melt and then cooling, the bloom disappears and leaves a bright, clean surface on the chocolate, which then becomes resistant to blooming (5). By studying the dilation curves of cocoa butter as well as the hardened vegetable fat which had been plotted on the same graph, it was noticed that bloom appears on the chocolate surface at that temperature where these dilation curves cross, thus indicating an internal stress (3).

However we are not discussing the cause or prevention of bloom but the composition of the bloom fat. All of the conflicting references given indicate that a thorough study is called for and that this study should begin by knowing with what we are dealing. What is *bloom?* that is, what is it composed of? Is it pure cocoa butter? Is it a specific triglyceride of cocoa butter? Or is it a complex mixture in which other ingredients of the chocolate are combined?

It would seem that these questions should be answered before any definite preventive can be recommended. Certainly none of the recommendations so far advanced by authorities in the field will actually stop bloom formation. Some of these recommendations are definite alleviators, but to date none are cures.

Experimental

Chocolate Coating. The composition of the chocolate coating used in all of the tests was the same, and the formula is as follows: cocoa liquor, 40%; sugar, 48%; cocoa butter, 10.17%; lecithin/C. b/1:1, 0.45%; vanilla paste, 1.35% and vanillin, 0.03%. The cocoa liquor was a blend of three different kinds of Central American cocoa beans. The average fat content of the chocolate was 32.3%. Although the chocolate which was used was prepared at different times from different batches of chocolate mass, the formulation of the chocolate described above was maintained throughout the tests.

Centers. The centers were obtained from a commercial candy manufacturer and were taken directly from the production line of the chocolate plant. Nine centers, representing three classifications, were used. The high oil-containing centers were roasted hazel nuts and roasted almonds. Peppermint cream, vanilla cream, coconut cream, and marshmallows represented the high moisture-containing centers. A shell candy, chocolate parfait, as well as two hard candies, represents the low moisture-containing centers.

Storage. The various coated centers were taken directly from the production line and were placed in fiber cases in regular layers. A plastic-coated paper was placed between each layer. Each case contained approximately five to six kilograms of candies. These cases in turn were placed in cardboard cartons and stored at a temperature of 20–21°C. The rate of blooming of the chocolate depended upon the type of center used. The storage times for the various chocolate-coated pieces are shown in Table I.

Isolation of Fat. To obtain a representative sample of bloom fat from the surface of the bloomed candies the procedure was as follows. Soft nylon brushes ½-in. wide were used for brushing off the grey surface-layer (bloom) from the bloomed candies. Extreme care was taken to keep the bloom from being contaminated with other fats. The candies were always handled with rubber gloves. Where air bubbles had formed on the surface of the candies, those area were not touched so that chipping of the coating and contamination of the sample was avoided. Approximately one-half of the bloom was brushed from each candy because more brushing would possibly lead to contamination of the sample. Only 10 to 15 pieces could be brushed before the brush became saturated with bloom fat and had to be replaced. The brush was cleaned by soaking in commercial hexane and then dried by air evaporation. Two brushes were used alternately in order to utilize the drying period of the brushes. The bloom, as well as the hexane washings, was then placed in a micro-Soxhlet and extracted with commercial hexane for five days. The hexane was then removed at room

TABLE I

Type of candies	Age of candies	Wt. of brushed candies	Coating % of candy	Wt. of coating	Wt. of fat in coating	Bloom fat		
						Wt. in brushed bloom	Wt. in total bloom [a]	% of Coating fat
		kg.		*kg.*	*kg.*	*g.*	*g.*	
Coated hazelnuts	3 yrs.	2.70	43.17	1.17	0.378	0.9	1.8	0.476
Coated almonds	2 yrs.	2.20	53.91	1.19	0.384	0.9	1.8	0.476
Peppermint cream	1 yr.	18.55	36.48	6.77	2.187	9.0	18.0	0.821
Vanilla butter cream	9 mos.	38.90	38.63	15.03	4.855	3.7	7.4	0.152
Coconut cream	8 mos.	14.90	43.33	6.46	2.087	1.8	3.6	0.172
Marshmallow	7 mos.	14.05	56.39	7.92	2.558	1.6	3.2	0.125
Hard candy I Lime brittle chip	1 yr.	13.64	57.14	7.79	2.516	3.5	7.0	0.278
Hard candy II Lemon coconut	1 yr.	12.52	51.57	6.46	2.087	7.9	15.8	0.757
Chocolate parfait	2 yrs.	8.75	77.21	6.76	2.183	1.2	2.4	0.110

[a] Calculated provided that it was possible to brush off only 50% of the existing bloom fat.

temperature under reduced pressure.

The coating fats were obtained from the same candies from which the bloom had been brushed. A representative sample of the coating was cut from the candy with a knife. Approximately 75 pieces of each candy were treated in this manner to obtain sufficient oil for analyses. The method of extraction of the fat from the coating was identical with that used for the bloom fat.

In the case of the hazelnut center all coating was removed, and the nuts were ground in a mortar and extracted in a micro-Soxhlet for five days, reground, and re-extracted for two more days. The solvent was removed at room temperature under reduced pressure to recover the hazelnut fat.

All of the above fat samples were stored at −15°C. until analyzed. The nonfat residue of the bloom had a grey appearance and formed approximately one-third by weight of the brushed bloom.

Description of Samples. The description of the centers, together with the ingredients of the centers, is given in Table II.

TABLE II

Description of Centers

Type	Ingredients
Hazelnut	Roasted hazelnuts
Almond	Roasted almonds
Peppermint cream	Sugar, invert sugar, corn sirup, water, frappe, invertase, citric acid, peppermint oil, and gelatin
Vanilla butter cream	Sugar, invert sugar, water, butter, esters, lecithin, casein, alcohol, starch, vanillin, citric acid, propylene glycol, BHA, and NDGA
Coconut cream	Sugar, invert sugar, corn sirup, water, frappe, invertase, citric acid, vanillin, coconut flavor, coconut, and NDGA
Marshmallow	Sugar, invert sugar, corn sirup, water, gelatin, frappe, and vanillin
Hard candy I Lime brittle chip	Sugar, invert sugar, corn sirup, water, vegetable fat, lime oil, citric acid, and green color
Hard candy II [a] Lemon coconut	Sugar, dextrose, corn sirup, invert sugar, water, lemon peel, apricots, pectin, citric acid, vegetable fat, coconut, frappe, salt, vanillin, and coconut flavor
Chocolate parfait	Chocolate, mint oil, invert sugar, condensed milk, vanillin, sodium benzoate, sucrose, and water

[a] Lemon coconut-filled shells.

In the case of mint candies, crystals appeared above and below the candies on the paper in which they were stored. These candies had much more, and larger bloom crystals than candies with other centers. The bloom which appeared on the paper was collected in a manner similar to that previously described, and fat was extracted in the same manner and will be called "surrounding" fat.

Methods of Analysis

Iodine Value. The iodine values were determined by the American Oil Chemists' Society modification of the Wisj method, Cd 1-25 (1).

Polyunsaturated Acids. The percentages of linolenic acid, linoleic acid, oleic acid, conjugated triene, and conjugated diene were determined by the American Oil Chemists' Society ultraviolet spectrophotometric method Cd 7-48 (1). The saturated acids were determined by difference. The linolein and olein content was calculated from the respective fatty acid composition.

Hydroxyl Values. The percentage of hydroxyl was determined by the method described by Ogg *et al.* (13).

Saponification Equivalents. The saponification equivalents were determined as follows. Approximately 75-100 milligrams of fat were saponified under reflux for one hour with 10 milliliters of 0.1 normal alcoholic potassium hydroxide. Ten milliliters of 0.1 normal hydrochloric acid (of slightly higher normality than the 0.1 normal alcoholic potassium hydroxide) were added along with some neutralized alcohol containing phenolphthalein indicator. The solution was boiled to expel carbon dioxide, and the excess acid was back-titrated with 0.05 normal alcoholic potassium hydroxide while the titration flask was swept out with a vigorous stream of carbon dioxide-free air.

Results and Discussion

From the results in Table I it can be seen that the high-moisture centers tended to bloom sooner than the candies with low-moisture centers. A high oil-content in the centers delayed blooming. There is practically no moisture present in high oil-content centers, consequently there is an apparent correlation between the rate of blooming and the moisture content in the center. Since this correlation does not hold true in every case, other factors affect blooming rate in addition to moisture. The total weight of brushed candies, as well as the weight of the coating and the weight of the fats in the coating, are given in Table I, also the total weight of bloom fat obtained and the percentage of fat in the coating which appeared as bloom. No correlation can be made between the amount of bloom fat and the coating fat on a weight basis. This might be expected since blooming in chocolate is a surface phenomenon, and the total surface-area of the candies would be a larger factor than the weight of the fat in the coating in determining the extent of blooming.

Data assembled in Table III show that iodine values of the bloomed fat range from 1.0 to 4.1 units lower than those of the coating fat. There does not seem to be any correlation between the type of center and the decrease in iodine value. In fact, the differences in iodine values between the bloomed and the coating fats agree with the results obtained by Neville *et al.* (12). These workers obtained their bloomed fat from a slab of stored cocoa butter, and no cocoa solids or sugar were present. Thus it can be concluded that blooming is a fat phenomenon and that the mechanism of blooming is not affected by the presence of cocoa solids or sugar although the rate of blooming may be affected by these materials.

The fatty acid analyses calculated on a glyceride basis show that the bloomed fat is lower in olein and linolein content, and higher in the saturated acid glycerides. This difference in composition is evident in all cases. The decrease in linolein content was 0.5–1.3%, and the olein content decrease was 0–2.3% while the saturated glycerides increased by 1.5–3.2%.

Results for the fats from coated hazelnuts show that the oil from the nut does not penetrate through the coating to the surface to produce bloom. Comparison of the coating fat of this sample with the

TABLE III
Analyses of Coating and "Bloomed" Fats

Centers	Fatty Acid Composition[a]							
	Iodine value	Linolenin	Linolein	Olein	Saturated glyceride	Conjugated triene[b]	Conjugated diene	Sapon. no.
Oil-containing:		%	%	%	%	%	%	
Hazelnut								
Coating	37.9	.14	3.4	36.6	60.1	.0009	.0869	208
Bloom	34.4	.10	2.3	35.0	62.8	.0003	.0718	.....
Nut	75.0	.05	5.9	74.9	19.2	.0000	.152	192
Almond								
Coating	38.2	....	4.5	35.0	60.5	.....	.....	194.5
Bloom	35.8	....	4.0	33.6	62.4	.....	.....	195.2
High moisture:								
Peppermint cream								
Coating	38.0	.20	3.7	35.9	60.4	.0065	.0853	198
Bloom	35.7	.18	3.0	34.7	62.3	.0015	.0680	195
Surroundings	32.4	.07	2.2	32.8	65.0	.0015	.1257	198
Vanilla cream								
Coating	38.0	.22	3.5	36.2	60.2	.0071	.0774	185
Bloom	33.9	.14	2.2	34.4	63.4	.0017	.0512	189
Coconut cream								
Coating	38.0	.16	3.9	35.7	60.4	.0058	.0807	204
Bloom	34.8	.10	2.8	34.8	62.8	.0034	.0364	192
Marshmallow								
Coating	36.4	.11	3.2	35.4	61.5	.0169	.0657	192
Bloom	32.9	.10	2.3	33.1	64.6	.0039	.0998	.....
Low moisture:								
Hard candy I								
Coating	35.6	.12	3.2	34.5	62.4	.0119	.0799	209
Bloom	33.1	.07	2.6	32.9	64.5	.0116	.0735	190
Hard candy II								
Coating	36.6	.14	3.3	35.3	61.4	.0084	.0637	195
Bloom	34.6	.10	2.6	34.6	62.8	.0042	.0350	196
Shell candy—Choc. parfait								
Coating	36.2	.18	3.1	35.0	61.8	.0069	.0595	191
Bloom	35.2	.17	2.6	35.1	62.3	.0010	.0639	192

[a] Calculated as glycerides.
[b] The data for linolenin, conjugated diene, and conjugated triene is reported as obtained although it is realized that they may be artifacts arising from the oxidation of linolein.

average analyses of the coating fats of the other samples shows that the fat is similar to the average. If the hazelnut oil had penetrated into the coating, a marked increase in the olein content of the coating fat should be noted as this oil has a very high olein content. The bloomed fat is also no higher in olein content than the maximum of 35.1% found in bloomed fat from the shell-coated parfait, providing evidence that migration of oil from nutmeat centers is not responsible for bloom. It is known that, in general, chocolate pieces with nut centers bloom sooner than do pieces with other centers. Possibly other factors such as osmotic pressures or surface tensions at the center coating-interface may account for the relative rates of blooming.

The percentage of hydroxyl was determined on three series of fats in order to determine the effect of oxidation on blooming. In the peppermint cream series the coating fat analyzed zero percentage of hydroxyl, the bloom fat zero percentage, and the surrounding fat 0.1%. In the vanilla cream series the coating fat analyzed 0.12% hydroxyl and the bloom fat 0.07%. In the coconut cream series the coating fat analyzed 0.46% hydroxyl and the bloom fat zero percentage. From these analyses it is evident that hydroxyl containing fatty oxidation products do not enter into the fat-bloom picture.

The sample (peppermint cream, surroundings) was carried along in this series of analyses because in this case the bloom was transferred to the adjoining paper fillers, thus completely apart from the coating surface. This was done in order to determine whether the peppermint oil in the centers had caused this phenomenon. The results show that this fraction had a lower iodine value than the bloom fat. The linolein and olein content of this fraction was slightly lower than the bloom fat, and the saturated glyceride content was slightly higher. These results may be interpreted to mean that the peppermint oil in the center is not present in the bloom itself but that it may act as a carrier for the bloom fat because of its high volatility.

The average fatty-acid composition of the chocolate coatings of the nine candies, calculated on a glyceride basis, is 3.5% linolein, 35.5% olein, and 61.0% saturated acid glycerides while the average fatty acid composition of the bloom fat, calculated on a glyceride basis, is 2.7% linolein, 34.2% olein, and 63.1% saturated acid glycerides. A difference in in the average fatty acid composition, on a glyceride basis, between the coating and the bloom fat is 0.8% linolein, 1.3% olein, and 2.1% saturated acid glycerides. Based on the original coating fat composition, the percentage decrease in olein content is 3.7%, and a corresponding percentage increase in saturated acid glycerides is 3.5%.

Summary

The composition of the fat which has bloomed in chocolate has been investigated. There is evidence that the type of center which is coated with chocolate has no effect upon the fatty-acid composition of the bloom fat. The rate of blooming however was found to be affected by the center. The theory that the oils in coated nuts migrate to the chocolate surface to cause fat bloom has been disproved. Comparison of the fatty acids present in the bloom fat with respect to the coating fat show a decrease in the unsaturated acids and an increase in the saturated acids. There is evidence that hydroxyl containing oxidation products of the fatty materials in the chocolate are not present in the migrated fat.

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Selective Fixation of Deleterious Phosphatidic and Pigment Materials in Commercial Processing to Improve Quality of Cottonseed Oil and Meal[1]

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IN A PREVIOUS REPORT (4) on a commercially operating, integrated cottonseed oil mill and salad oil plant a process was described for producing a quality, dust-free, solvent meal and a salad oil with excellent keeping quality, flavor, and chill test (5). Since these data were presented, additional work has been done on evaluating the specific effect each step of processing has on the meal and on the oil. These data comprise the subject matter for the present report.

As a basis for comparing quality of meal and oil in various stages of processing the following criteria were arbitrarily set up:

Meal

1. Free gossypol (1)
2. Nitrogen solubility in 0.02N NaOH (10)
3. Available gossypol units—A.G.U. (7).

In addition to the analyses enumerated above, all meal samples were analyzed for moisture, oil, crude protein, and pH. The latter measurement was determined by stirring 20 g. of meal for 10 seconds in a Waring Blendor with 200 ml. of distilled water. pH was read on slurry with a Beckman pH meter.

The criteria for evaluating the quality of the crude oil through the various stages of processing and also for determining the effect of exposure to sunlight and air on crude cottonseed oil were:

Oil

1. Moisture and volatile matter
2. Free fatty acids
3. Lovibond color of 1-in. column of crude oil
4. Chromatographic loss.

Analysis of the source material and processing conditions under which the meal and oil described in this report were produced follows:

Seed Variety: Acala 4-42
Seed Analysis

	%		%
Moisture	8.2	F.F.A.	0.5
Oil	19.8	Total lint	12.2
Ammonia	4.16	Grade	110.0
Free Gossypol	0.97 (moisture- and oil-free basis).		

The cottonseed meats with added hulls to control the protein to 41% were flaked in five-high rolls to 0.016 in. and cooked in five-high stack cookers. Moisture content of cooked meats at the cooker discharge was 12.6%, temperature of meats at cooker discharge, 208°F.(98°C.). Granular soda ash was added to the cooked meats at the rate of 0.4% of the weight of the cooked meats prior to prepressing.

The prepressed flake averaged 13.5% residual oil, and the temperature of prepressed flake at screw-press discharge was 207°F.(97°C.).

The highest temperature to which the crude oil was exposed was 210°F.(99°C.) in the cooking and prepress stages, the highest temperature to which the meal was exposed, 235°F.(113°C.) at the final, meal-dryer discharge.

The data in Table I show the effect each stage of processing has on the meal. Commercially processed, cottonseed meat-hull mixtures normally have an oil content of approximately 30%. Cooked meats before and after addition of soda ash and prepressed flakes were extracted in the laboratory with n hexane to obtain the meals shown in the first three columns in Table I. The meals from the extractor, tube dryer, and dryer and toaster were used as they came from the plant except that the extractor meal was air-dried to remove the hexane.

Table I shows a normal and reasonable reduction of gossypol in cooking, in the prepressing step after the addition of solid soda ash, and in the solvent-extraction and meal-drying stages (11). This is especially noteworthy because miscella-refined soapstock is added to the second of five tube-dryers in series. This soapstock has a slight excess of caustic soda and supposedly contains considerable amounts of gossypol (2) which has been removed from the oil by the alkali-refining processes (6). Yet the data show a normal decrease in free gossypol and also a decrease in pH in spite of the addition of the alkaline soapstock from miscella refining. This decrease in pH is attributed to the presence of residual soda ash from the initial treatment of the meats subsequent to cooking.

A.G.U., or Available Gossypol Units, is a combined biological and chemical assay of the gossypol present in cottonseed meal, which will combine with cephalin in egg yolks to form a cephalin-gossypol complex that is related to egg-yolk discoloration (7).

Dr. Grau and co-workers at the University of California are responsible for developing this new tool for evaluating a cottonseed meal with respect to pos-

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