"adulterant" was added to 30 different butter samples. The results plotted in Figure 2, *b*, show that 10% may be easily detected. As a test of the method, the adulterant was added at the 2 to12% level to 36 samples, which were then mixed with 69 pure samples as unknowns.

The results are summarized in Table II. In every case where adulteration was not detected, the plot for the starting pure butter was to the left of the least-squares line, and the level of adulteration was less than 7%.

In addition to the adulterant fat, 27 other hydrogenated fats were added to one butter sample at the 10% level, with the results shown in Figure 2, *c*. Table III lists these fats, their iodine values, and an estimated level of detection in a butter whose plot falls on the least-squares line.

Range of Concentration of cis-trans Conjugated Dienoic Acids and Isolated trans Acids. Pure compounds were not available for estimation of extinction coefficients under our conditions. However, two samples at the extremes of the range encountered were dissolved in carbon disulfide, and the infrared spectra obtained using, as reference, a solution of olive oil which appeared to be free of conjugated or unconjugated trans double bonds. Using the absorptivity of 0.288 liter per gram cm. at 948 $cm.^{-1}$ found by Chipault and Hawkins (*6*) for methyl esters, the range for the conjugated *cis-trans*-diene was found to be 2.1 to 4.5%. Using the absorptivity of 0.460 liter per gram cm. for the trielaidin reported by Callen and Pace (*5*), the range for isolated trans unsaturated acids was found to be 5.8 to 12.0%. The ratio of the concentration of isolated trans to conjugated trans unsaturation is about 2.7.

When 10% of a hydrogenated fat is added, the ratio is changed to 3.1 to 3.8, with the exact value dependent on the trans acid content of the adulterant and of the butter.

Suggested Mechanism for Formation of cis-trans and trans Unsaturation in Butter Fat. It has been suggested (*9, 17*) that butter contains little, if any, linoleic acid (*cis*-9, *cis*-12) normally found in seed fats. Apparently the cow, in passing linoleic acid in the diet through its system to the milk, isomerizes some linoleic acid to a cis-trans conjugated dienoic acid, which then undergoes biological hydrogenation in its rumen to form a trans isomer of oleic acid such as vaccenic acid (*2, 8, 14, 15*). The first isomerization would be the rate-controlling step and would establish the amounts of these components.

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FOOD DISCOLORATION

Browning in Dried Fruit Products: Non-enzymatic Browning and Its Effect on the Carotenoids in Qamareddeen, a Dried Apricot Pulp

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A study of the effects of blanching, sulfurization, and moisture level on the development of browning and the levels of lycopene and β-carotene in dried apricot pulp has demonstrated that an improved product is obtained when the fruit is steam-blanched for 3 minutes and the pulp is sulfurized with 2000 p.p.m. of sulfur dioxide, then dried to 25% moisture content.

One of the favorite dried fruit products in Middle Eastern countries is Qamareddeen, an apricot pulp dried in the form of thin sheets. A local variety of apricots known as Klabi is preferred for making this product.

The preparation of Qamareddeen is often carried out on a relatively small scale. The fruit used is usually of high fiber content and low eating quality, often overripe windfalls. After being washed, the fruit is mashed in straw baskets, and the pulp is spread in depths of 3 to 10 mm. on wooden trays that have been thoroughly oiled. The trays are then placed in the sun for drying, until the moisture level reaches 20 to 25%. A few producers sulfurize the apricot pulp by mixing with a dilute solution of sodium metabisulfite. The sulfuring level is critical in its influence on flavor, as the dried product is often consumed without reconstitution. The dried pulp is wrapped in yellow cellophane film or parchment paper and stored at room temperature. Considerable browning commonly occurs during storage with consequent adverse effect on quality.

The browning of dried apricots has been studied extensively by Stadtman and his associates (*8–10*), who found that sulfurization extended the storage life

Table I. Effect of Blanching, Sulfurization, and Moisture Level on Browning and Carotenoids in Qamareddeen

Sample Code	Sulfurous Acid Content, P.P.M.				Absorbance of Brown Pigments at 440 Mμ				Lycopene Content, γ/G.				β-Carotene Content, γ/G.			
	Storage Period, Months															
	0	3	6	9	12	0	3	6	9	12	0	3	6	9	12	0	3	6	9	12
Control 10	...	...	...	...	...	0.08	0.18	0.32	0.62	0.96	12.2	7.8	5.9	4.7	4.6	46.3	31.2	25.4	23.5	23.2
Control 25	...	...	...	...	...	0.08	0.19	0.36	0.65	0.99	13.7	7.2	6.2	4.9	4.4	45.8	33.0	26.4	22.6	23.9
A 10	...	...	...	...	...	0.08	0.16	0.38	0.60	1.00	11.9	10.1	8.3	7.2	7.1	44.2	40.2	36.3	33.4	32.1
A 25	...	...	...	...	...	0.08	0.17	0.37	0.62	0.98	12.3	9.8	9.2	6.9	7.0	46.1	39.8	34.7	33.3	32.8
B 10	680	620	580	540	470	0.08	0.12	0.14	0.28	0.66	12.1	10.7	8.2	6.8	6.1	45.7	40.5	34.6	30.4	29.0
B 25	820	780	740	670	580	0.08	0.13	0.16	0.29	0.71	12.8	10.2	8.5	7.4	6.7	46.4	42.4	34.8	30.5	29.0
C 10	1430	1320	1240	1120	820	0.08	0.13	0.16	0.21	0.43	12.7	11.8	10.1	8.3	7.8	48.3	41.3	38.2	33.5	32.2
C 25	1840	1640	1520	1430	1130	0.08	0.14	0.15	0.23	0.57	12.2	12.0	10.7	8.7	7.3	48.5	40.7	38.0	34.0	33.4
D 10	1170	1110	1040	930	730	0.08	0.11	0.13	0.19	0.27	13.4	12.4	11.2	9.7	9.3	47.2	40.0	37.8	38.6	38.0
D 25	1300	1200	1120	990	850	0.08	0.11	0.15	0.21	0.29	13.2	11.9	10.7	9.5	9.7	48.8	41.0	38.8	39.4	37.9
E 10	2450	2320	2160	1950	1780	0.08	0.10	0.13	0.17	0.22	12.6	12.4	10.5	9.6	9.1	45.5	39.6	38.2	39.6	38.9
E 25	2760	2480	2390	2280	2060	0.08	0.11	0.15	0.16	0.27	13.3	12.1	10.9	9.9	9.8	47.1	40.2	38.3	38.6	38.6

of dried apricots, but did not prevent the occurrence of browning. Absence of oxygen from the pack as well as reduction of storage temperature offered some protection against browning changes. The browning reactions involved seemed to be of the Maillard type, where the amino groups of proteins react with the carbonyl groups of sugars giving rise to intermediates which, upon polymerization, yield melanoids, the brown pigments. Changes in the carotenoids of apricots during browning have not been investigated.

The Maillard-type browning reactions were shown by Wolfrom and Rooney (*11*) to be at a minimum at both high and low moisture concentration and to have a maximum value at an intermediate moisture level of about 30%. Much work has been carried out to elucidate the mechanism of browning in processed foods as well as in model systems. Excellent reviews on the subject have been published by Stadtman (*7*) and Hodge (*4*).

The work reported here was undertaken in an attempt to define conditions which producers could utilize in preparing Qamareddeen with better storage qualities. The effect of blanching, sulfurization, and moisture levels on the browning changes and the levels of carotenoids were investigated at intervals during 1 year of storage.

Experimental

Twelve lots, of 5 kg. of apricots each, were subjected to the following treatments:

Lots A 10 and A 25. The fruit was blanched in live steam for 3 minutes, then passed through a pulper-finisher. The pulp was dried in a forced-draft oven at 180° F. for the first 4 hours, then at 160° F. until the moisture level reached 10% for A 10 and 25% for A 25.

Lots B 10, B 25, C 10, and C 25. The fruit was not blanched, but the pulp was sulfurized by mixing with a 6% sulfurous acid solution to produce levels of sulfur dioxide of 2000 p.p.m. for B 10 and B 25, and of 4000 p.p.m. for C 10 and C 25. The pulps were then dried to the corresponding moisture level.

Lots D 10, D 25, E 10, and E 25. The fruit was blanched in live steam for 3 minutes and the pulp was mixed with 6% sulfurous acid to give 2000 p.p.m. of sulfur dioxide in D 10 and D 25, and 4000 p.p.m. in E 10 and E 25. The pulps were then dried to the corresponding moisture levels.

Lots Control 10 and Control 25. The fruit was pulped and the pulp dried to the corresponding moisture level.

The dried pulp in each lot was divided into five equal portions and packed separately in yellow cellophane bags, then stored at room temperature for 1 year. At 3-month intervals, the different lots were tested for sulfur levels, degree of browning, and carotenoid levels.

The sulfur level in the pulp was determined by the Monier-Williams method (*1*).

The degree of browning was determined according to Stadtman (*10*) by extracting the pigments from 2 grams of ground, dried pulp with 70 ml. of 50% alcohol by shaking gently for 16 hours. The extract was diluted to 100 ml. and filtered. The absorbance of the filtrate was measured at 440 mμ, which has been reported to be a suitable wave length for measuring the brown pigments (*6*). The absorbance values were taken as an indication of the extent of browning in the sample.

The carotenoids of apricots, β-carotene, γ-carotene, and lycopene (*2*) were extracted, chromatographed, and their amounts determined as outlined by Lime *et al.* (*5*). The β-carotene and the γ-carotene were eluted, as one fraction, with 10% acetone in hexane and determined as β-carotene. The lycopene was eluted with 5% methanol in hexane and its absorbance was compared with that of a lycopene standard, prepared from tomato paste (3).

The absorbance values in the determinations of carotenoids and brown pigments were measured with a Beckman spectrophotometer, Model DU.

Results and Discussions

The sulfurized pulps lost 30 to 65% of their sulfur content upon drying, as indicated in Table I. Pulps that were blanched retained more of their sulfur content during drying and storage than did those which were not blanched. The samples dried to 10% moisture content retained about as much of their sulfur as did those dried to 25% moisture.

The degree of browning seemed to vary inversely with the sulfur content of the pulp. While blanching did not offer much protection against browning, sulfurization did bring about a definite and proportional decrease in the rate of browning. This is in agreement with Stadtman's findings (*10*) for dried apricots. However, the combination of blanching and sulfurization proved to be more effective than either process alone in retarding browning in Qamareddeen. This may be attributed to the removal of gases, including oxygen, from the tissues during blanching. Thus, the oxidation of sulfur dioxide to sulfate, which is ineffective in retarding browning, would be partially eliminated.

Blanching and sulfurization were each effective in reducing the loss of carotenoids in the dried pulp during storage.

The combination of both processes, however, still further reduced the loss of the carotenoids. Lycopene and β-carotene behaved similarly during storage.

It is evident from Table I that there was no difference in the development of browning nor in the lycopene and β-carotene contents between the two moisture levels tested.

The data obtained in the course of this investigation indicate that a combination of blanching and sulfurization would improve greatly the storage quality of Qamareddeen. At the sulfurization level of 4000 p.p.m. of sulfur dioxide, the taste of sulfur was detectable, when the pulp was consumed without reconstitution. In this respect, the 2000 p.p.m. sulfur dioxide level proved more desirable. On the other hand, drying the pulp to a 10% instead of a 25% moisture content produced slight off-flavor and did not show any superiority in storage quality.

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RADIATION PRESERVATION OF FOODS

Carbonyl Compounds of Irradiated Meats

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In irradiated beef, pork, and chicken, iso-octane–soluble carbonyls come from the lipide and aqueous-soluble carbonyls come from the protein. Irradiation of beef, pork, chicken, and beef liver gives rise to a wide variety of long-chain aldehydes and ketones. They appear to be derived from plasmalogens and other lipides, but the precursor-product relationship appears complex. Carbonyls decrease during storage and cooking.

CARBONYL COMPOUNDS produced by irradiation of meat are important in determining the characteristic odor and flavor of irradiated meat (*1, 8*). The slower rate of gastrointestinal absorption of irradiated lard may be explained by the presence of carbonyls, which delay gastrointestinal absorption and inhibit pancreatic lipase (*10*). The two main groups of precursors for the formation of carbonyls are the lipides and the proteins and amino acids. The mechanism for the production of carbonyls from lipide precursors by aerobic irradiation is well known. Scission products including carbonyl compounds result from lipide peroxidation. This mechanism is based upon that of the autoxidation of lipides, and carbonyls have been shown to result from aerobic irradiation of meat fats and pure lipides (*2, 13*).

In our previous research (*5*), beef and pork irradiated in the presence of oxygen developed relatively high lipide peroxides and iso-octane–soluble carbonyl compounds. In contrast, beef and pork irradiated under anaerobic conditions of pure nitrogen did not produce large amounts. Thus, irradiation in the presence of oxygen initiates free-radical lipide peroxidation, which at the dose level proposed for pasteurization or sterilization gives unacceptable levels of oxidative fat rancidity. This is the main reason why meat should be irradiated under anaerobic conditions. Batzer *et al.* (*1*) likewise studied carbonyl compounds produced during aerobic irradiation of beef and pork fat. They found a greater amount of water-soluble carbonyl produced than lipide-soluble carbonyl. The mechanism by which small amounts of carbonyl are produced when lipides are irradiated under anaerobic conditions has not been defined. Carbonyls may arise from the protein and amino acid portion of meat by several mechanisms (*3, 4*).

This paper reports research defining the relative amount of carbonyl compounds derived from the lipide and protein portions of meat and the composition of iso-octane–soluble carbonyl compounds produced by anaerobic irradiation of beef, pork, chicken, and beef liver.

Experimental

Meat Samples and Irradiation. All the meats used as samples were purchased in large quantities from local sources and finely ground and mixed to prepare representative samples. The various meats and meat components were packed in No. 2 enameled cans, and evacuated and gassed four times with pure nitrogen. Transportation for irradiation was at dry ice temperature. Irradiation was at 20° C. with 0.6- to 2-M.e.v. γ-radiation from spent fuel rods at the Materials Testing Reactor, Arco, Idaho. Subsequently, all samples were held at −20° C. prior to analysis.

For measurement of iso-octane– and acid-soluble carbonyls in the first experiment, beef round, boned pork chops, and the muscles of chicken thighs were used. For separation into the com-

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