Preliminary Studies on the Fate of Sugars and Amino Acids in Chips Made from Fresh and Stored Potatoes

THOMAS J. FITZPATRICK, EUGENE A. TALLEY, and WILLIAM L. PORTER

Eastern Regional Research Laboratory, Philadelphia, Pa. 19118

A study of the changes in sugars and nitrogenous constituents of unstored Red LaSoda potatoes during chip frying revealed a loss of 67% of reducing sugar accompanied by a loss of 52% of amino and amide nitrogen. However, when chips were made from potatoes stored in the cold to increase the sugars sevenfold, the decrease of reducing sugar on frying was 85%, with a corresponding decrease of 85% in amino and amide nitrogen. The ratio of the decrease in nitrogen to reducing sugar was 5 to 4 μmoles. Twenty-four free amino acids and amides were identified and measured in these potatoes.

In addition to browning reactions catalyzed by enzymes and those due to caramelization, the most common browning reactions recognized in food technology are the carbonyl-amino reactions, including the reaction of reducing sugars and other aldehydes and ketones with amines, amino acids, peptides, and proteins.

Hodge (*5*), in his comprehensive review of the chemistry of browning reactions in model systems, proposes a scheme of reactions which involves sugar-amine condensation with subsequent Amadori rearrangement, followed by sugar and amino acid degradation, aldol condensation, and aldehyde-amine polymerization.

Anet and Reynolds (*1*) and Ingles and Reynolds (*6*) gave further substance to this hypothesis by the isolation of numerous amino acid–sugar reaction products from apricot and peach purées after several months' storage at room temperature and below. These compounds accounted for most of the 61% decrease in the free amino acids over the storage period. There was an accompanying decrease in reducing sugars of approximately 30%.

The solution to the problem of undesirable color development in potato chips, especially those involving potatoes held in cold storage, is closely linked to a knowledge of the reaction of the sugars and amino acids present at the time of dehydration by heat. Therefore, this study was undertaken to follow the changes in the complex pattern of free amino acids, amides, total sugars, and reducing sugars as affected by chip processing, low temperature storage, and chipping after storage.

Recently harvested potatoes not subjected to low temperatures were required. Only Southern potatoes conformed to this requirement at the time. Florida potatoes of the Red LaSoda variety were used because of the ready accumulation of reducing sugars by this variety during storage which accentuates browning possibilities. This single variety was used to develop techniques and to determine a basis for future studies now in progress. Recently Furuholmen *et al.* (*3*), on the basis of paper chromatographic results, reported the presence of nine amino acids in unnamed varieties of Florida potatoes. They state that this limited number of acids might be due to varietal differences or to cultural and environmental factors.

Experimental

Red LaSoda potatoes, freshly harvested in Florida, were purchased from a commercial source in April 1963. The average specific gravity was determined and the per cent solids was estimated by the Potato Chip Institute International (PCII) hydrometer method. Sampling was accomplished by placing the tubers in nine rows of equal length graduated from the largest tubers to the smallest. After recording the weights of each row (ca. 1200 grams), the nine samples were placed in separate containers. Two samples were retained for analysis of fresh potatoes and of chips made from fresh potatoes. The remaining samples were stored at 36° F. for 53 days. At this time, two additional samples were withdrawn for analysis of stored potatoes and of chips made from stored potatoes. Analyses on all samples included direct total solids, total and extractable nitrogen (by Kjeldahl), total and reducing sugars by the method of Spengler, Tödt, and Scheuer (*8*), and amino acids by the method of Spackman, Stein, and Moore (*7*) using a Phoenix Model K-5000 amino acid analyzer.

The fresh potatoes and the potatoes after storage were treated in the same manner. After being peeled 20 seconds in an abrasion peeler, the potatoes were slurried in an electric blender with sufficient alcohol to make the final concentration 70% by weight considering the original water in the potatoes estimated from the specific gravity measurement.

With the blender at low speed, samples were withdrawn for direct solids determinations by evaporation of moisture, for Kjeldahl nitrogen analysis, and for amino acid extraction. Amino acids were extracted according to the method of Talley, Carter, and Porter (*10*), which also removed all of the sugars present. Kjeldahl nitrogen, sugar, and amino acid determinations were run on these extracts.

Chips were prepared from the fresh and stored potatoes and analyzed in the following manner. All samples were peeled for 20 seconds in an abrasion peeler. An electric chipping machine was used to slice the tubers into chips 1 mm. thick. The chips were weighed and then fried at 350° F. for ca. 8 minutes until dehydration was complete. The additional time for complete dehydration (double that of commercial practice) was necessary because of the high ratio of potato slices to frying oil used in the basket-type fryer. Some chips were inadvertently overfried. After draining, the chip yield was determined.

An exact aliquot of macerated chips was made fat-free by Soxhlet extraction with Skellysolve B. The per cent solids was readily calculated from the extracted material remaining. Kjeldahl analyses were run on this fat-free preparation and

Table I. Solids and Nitrogen Content of Red LaSoda Potatoes and Chips[a]

Sample	% Solids		% Total N in Starting Material	% N	
	From sp. gr.	Direct		In extract	Extractable
Fresh potatoes	17.63	17.91	0.3238	0.2036	62.88
Chips from fresh potatoes	17.63	17.61	0.3059	0.1858	60.74
Stored potatoes	18.25	18.05	0.3343	0.2170	64.90
Chips from stored potatoes	18.30	18.30	0.3590	0.1950	54.30

[a] Calculated on fresh tuber basis.

Table II. Amino Acid Determination in Fresh and Stored Potato and Chip Extracts[a]

Amino Acid	Vol.[b]	Fresh		Stored		Amino Acid	Vol.	Fresh		Stored	
		Tubers	Chips	Tubers	Chips[c]			Tubers	Chips	Tubers	Chips[c]
Unknown[d]	40	0.14	0.53	0.86	0.34	Methionine	428	7.08	1.52	5.50	0.00
	42	0.25	0.41	0.47	0.33	Isoleucine	438	11.74	9.21	11.00	1.78
	47	0.19	0.45	0.13	0.34	Leucine	450	4.78	2.89	6.18	0.59
	55	0.24	0.13	0.22	0.32	Tyrosine	522	11.07	9.31	13.32	1.45
	68	0.13	0.00	0.08	0.14	Phenylalanine	532	12.40	6.09	9.32	0.88
	74	0.00	0.00	0.09	0.09	Unknown	555	0.00	0.00	0.00	0.55
	84	0.75	1.36	1.15	0.80	β-Alanine	588	1.85	1.01	2.05	0.74
Methionine sulfoxides	97	0.34	2.70	1.55	0.83	Unknown	90	0.00	0.00	0.00	0.07
Aspartic acid	124	13.25	14.61	10.26	3.53	Unknown	105	0.00	0.00	0.00	0.62
Threonine	133	7.62	3.87	8.84	0.79	Unknown	135	0.00	0.00	0.00	0.07
Serine	142	9.42	6.74	14.10	2.23	γ-Aminobutyric acid	179	29.99	13.51	39.82	3.67
Asparagine / Glutamine[e]	155	186.25	59.62	141.11	10.16	Ornithine	190	0.42	0.29	1.13	0.28
Unknown	160	1.41	0.00	0.33	0.00	Ethanolamine	218	0.00	0.00	0.50	0.00
Proline	191	5.43	4.83	6.00	1.03	Ammonia	225	23.45	39.80	34.38	28.62
Glutamic acid	205	21.82	3.85	19.66	0.67	Lysine	252	13.21	6.03	12.67	0.69
Glycine	245	5.16	3.38	4.86	0.82	Unknown	290	0.00	0.00	0.00	0.13
Alanine	260	12.46	9.05	22.70	4.96	Histidine	310	6.06	2.21	4.53	0.19
Unknown	289	0.52	0.80	0.45	0.00	Unknown	340	0.00	0.00	0.00	1.21
Valine	318	27.14	17.90	26.45	3.98	Unknown	362	3.19	1.71	2.37	0.58
Unknown + buff. change	390	0.39	0.25	0.66	0.72	Arginine	590	28.02	15.31	19.21	3.21
Unknown	395	0.00	0.08	0.00	0.00	Total, μmoles		446.17	239.45	421.95	77.41
Total μmoles of N/g. dry wt. (adjusted for multiple N compounds)								742.50	355.74	643.55	98.68

[a] Reported as μmoles/g. dry wt. Data are average of duplicate runs.
[b] Relative effluent volume. First series from long column. Second series from basic column.
[c] Chips made from stored potatoes.
[d] All unknown peaks calculated as leucine equivalents.
[e] Reported as asparagine.

samples equivalent to 50.0 grams fresh weight of potato were taken for the extraction of amino acids, which was accomplished as above (*10*). Kjeldahl, sugar, and amino acid determinations were run on these potato chip extracts.

The free amino acid extracts, equivalent to 50 grams fresh weight, were stored in 500.0-ml. aqueous alcohol solutions containing at least 20% alcohol. Amino acids were determined by vacuum-concentrating an aliquot to dryness—5.0 ml. for the acid and neutral amino acids, 10.0 ml. for the basic ones—and redissolving in 1.0 ml. of pH 2.2 sodium citrate buffer. This sample size gave optimum peaks on the automatic analyzer and the results could be directly equated to 0.5 and 1.0 gram, respectively, of fresh weight of potato.

Results and Discussion

There was a slight loss of weight in the tubers but scarcely a perceptible change in the solids content during the period of storage. This fact and the slight apparent gain in nitrogen after storage (Table I) are in agreement with findings previously reported (*2*). Exact duplication of results on original potatoes and on chips made from similar potatoes would be coincidence. Tubers in any given lot are not exactly similar in composition and vary within limits from each other.

The results of the amino acid determinations are reported in Table II. Several unknown peaks are listed and are reported as leucine equivalents. Ranging from less than 1 μmole to slightly more per gram of dry weight, many of these materials have effluent volumes, which from our preliminary studies correspond to those of amino acid–reducing sugar reaction products. The small quantity of these materials present in the extracts, even from potato chips having a high reducing sugar content, was probably due to the fact that frying to complete dehydration decreased the moisture level below that optimum (ca. 3 to 5%) for maximum formation of noncolored Amadori rearrangement products.

There was little loss in total nitrogen during the frying of these very dark chips. The extractable nitrogen also exhibited only a minor decrease. However, only a small amount of this extractable nitrogen was recovered by the amino acid analysis, indicating the formation of polymeric materials.

Of the broad spectrum of 24 identified amino compounds reported it is probable that only some of the decreases in the individual constituents after frying are due to reaction with reducing sugars and subsequent polymer formation. For example, the methionine sulfoxides present in the mixture are due to the oxidation of methionine during frying and subsequent sample preparation. The complete loss of methionine in the chips made from stored potatoes, however, cannot be accounted for by a corresponding yield of the sulfoxides. The amides, asparagine and glutamine, do not separate on the analyzer column; therefore, the total of these was reported as asparagine. The instability of glutamine on ion exchange resin columns is known and under these conditions a 25% loss is normal. Both amides, however, were sharply reduced in the frying process. It was suspected that this, in part, was due to cyclization of glutamine to pyroglutamic acid and conversion of asparagine to fumaramic acid (*11*). These compounds, being inactive to ninhydrin, were not measured.

In general, the conversion of the fresh potatoes to fried chips caused decreases, from mild to drastic, in all of the amino compounds reported except methionine sulfoxides, aspartic acid, and ammonia. (Increases in these three indicate formation of by-products.) This amino compound decrease amounted to 52.1% nitrogen (see Table III). There was an accompanying decrease of 66.6% of reducing sugars, with no significant change in sucrose (see Table IV).

During the storage period to increase the sugar content the apparent increase in total nitrogen of the tubers was hardly significant, but less than 75% of the extractable nitrogen could be recovered as free amino acids and amides. Even with this decrease in recovery, increases in several individual amino acids were apparent. Increases in the peaks for proline, alanine, γ-aminobutyric acid, and ammonia may be significant. However, an increase in peak size can be due to the formation of a new material with the same effluent volume as that of the original peak (*14*).

The sugar content of the potatoes increased as expected during this cold storage period. The results in Table IV indicate that the tenfold increase in reducing sugars was double that of sucrose, which increased about fivefold.

When the stored potatoes were converted into fried chips, the total nitrogen remained stable, while the extractable nitrogen was slightly lower (11.4%). The nitrogen recovered as amino acids and amides was drastically reduced. There was a loss of 84.7% of amino acid

Table III. Fate of Extractable Potato Nitrogen Due to Frying

Sample	N (Kjeldahl) μmoles/g. dry wt.	N (Kjeldahl) % loss on frying	Free Amino Acid Nitrogen[a] Recovery, μmoles/g. dry wt.	Free Amino Acid Nitrogen[a] % loss on frying	% N (Kjeldahl) as Free Amino Acids[a] Recov.	% N (Kjeldahl) as Free Amino Acids[a] Loss
Fresh potato extract	812.1		742.50		91.4	8.6
Fresh chip extract	741.0	8.8	355.74	52.1	48.0	52.0
Stored potato extract	858.7		643.55		74.8	25.2
Stored chip extract[b]	761.1	11.4	98.68	84.7	12.9	87.1

[a] Also includes amides and unknown peaks on analyzer. [b] Extract of chips made from stored potatoes.

Table IV. Fate of Potato Sugars Due to Frying

Sample	Sucrose Mg./g. dry wt.	Sucrose % loss on frying	Reducing Sugars[a] Mg./g. dry wt.	Reducing Sugars[a] μmoles/g. dry wt.	Reducing Sugars[a] % loss on frying
Fresh potato extract	13.43		9.73	54.01	
Fresh chip extract	13.15	2.0	3.25	18.04	66.6
Stored potato extract	70.58		91.13	505.83	
Stored chip extract[b]	64.37	8.8	13.42	74.49	85.3

[a] As fructose. [b] Extract of chips made from stored potatoes.

and amide nitrogen, accompanied by a loss of 85.3% of the reducing sugars, with less than a 9.0% decrease in sucrose. The actual ratio of the decrease in nitrogen to reducing sugar (as fructose) was in the order of 5 to 4 μmoles, respectively, per gram of dry weight of potato. The quantity of this nitrogen which combined directly with reducing sugars is not known. However, if we assume uniform losses of nitrogen from hydrolysis, cyclization, oxidation, etc., in the analysis of the potatoes and chips both before and after storage, the increase in reducing sugars on storage appears to be responsible for the additional 33% decrease in nitrogenous constituents when chips from these potatoes are fried.

Weast and Mackinney (*13*), working with a dark pigment from dried apricots stored for several years, indicated the combination of 1 mole of amino acid with 3 moles of sugar. It is commonly acknowledged, however, that in browning reactions, at least in those occurring in fruit, additional forces come into play. Haas and Stadtman (*4*) show that organic acids are involved, in addition to sugars and amino acids. The picture becomes more complex when a product such as the potato is subjected to frying at high temperatures which probably increase the speed and amplitude of the formation of the browning products.

Finally, the amino acid analysis of these potatoes confirms the presence of the amino acids found in Florida potatoes by Furuholmen *et al.* (*3*). Furthermore, the more sensitive analytical procedures employed revealed that these potatoes, qualitatively, contain the same full spectrum of amino acids found in potatoes grown in other areas of the country (*9, 10, 12*); however, some quantitative differences are present.

Literature Cited

(1) Anet, E. F. L. J., Reynolds, T. M., *Australian J. Chem.* **10,** 182 (1957).
(2) Fitzpatrick, T. J., Talley, E. A., Porter, W. L., Murphy, H. J., *Am. Potato J.* **41,** 75 (1964).
(3) Furuholmen, A. M., Winefordner, J. D., Dennison, R. A., Knapp, F. W., J. AGR. FOOD CHEM. **12,** 112 (1964).
(4) Haas, V. A., Stadtman, E. R., *Ind. Eng. Chem.* **41,** 983 (1949).
(5) Hodge, J. E., J. AGR. FOOD CHEM. **1,** 928 (1953).
(6) Ingles, D. L., Reynolds, T. M., *Australian J. Chem.* **11,** 575 (1958).
(7) Spackman, D. H., Stein, W. H., Moore, S., *Anal. Chem.* **30,** 1190 (1958).
(8) Spengler, O., Tödt, F., Scheuer, M., *Z. Wirtschaftsgruppe Zuckerind.* **86,** 130, 322 (1936).
(9) Talley, E. A., unpublished results.
(10) Talley, E. A., Carter, F. L., Porter, W. L., J. AGR. FOOD CHEM. **6,** 608 (1958).
(11) Talley, E. A., Fitzpatrick, T. J., Porter, W. L., *J. Am. Chem. Soc.* **81,** 174 (1959).
(12) Talley, E. A., Fitzpatrick, T. J., Porter, W. L., 48th Annual Meeting, Potato Association of America, Idaho Falls, Idaho, July 1964.
(13) Weast, C. A., Mackinney, F., *Ind. Eng. Chem.* **33,** 1408 (1941).
(14) Zacharius, R. M., Talley, E. A., *Anal. Chem.* **34,** 1551 (1962).

Received for review June 25 1964. Accepted September 30, 1964. Work performed at Plant Products Laboratory, Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Philadelphia, Pa. Mention of commercial products does not imply that they are endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.

FOOD COLOR STABILITY

Factors Affecting Oxidative Stability of Carotenoid Pigments of Durum Milled Products

LELAND DAHLE

Research Laboratory, Peavey Co. Flour Mills, Minneapolis, Minn.

The combined effect of lipoxidase, tocopherols, and free fatty acids on the oxidative stability of the carotenoid pigments of durum milled products was investigated. Free polyunsaturated fatty acids, which increase on the aging of wheat and flour, play a significant role. Tocopherols, if present in sufficient quantity, can influence oxidative pigment stability, and lipoxidase alone is an inadequate criterion by which to predict yellow pigment loss during macaroni and spaghetti processing.

THE carotenoid pigments of durum milled products (semolina and flours) are mainly responsible for the yellow color of macaroni and spaghetti. A bright yellow color is a mark of quality for the consumer and thus is an object of concern to the macaroni processor. The carotenoid pigments consist primarily of xanthophylls, with small amounts of xanthophyll esters and carotenes. The xanthophylls have been found to be mainly lutein and taraxanthin (*7*). These pigments are subject to oxidation by a coupled reaction involving the oxidation of polyunsaturated fatty acid lipids. The preponderant fatty acid present in flour lipids is linoleic, representing about 60% of the total fatty acids (*3*).

When a carotene-linoleate mixture is allowed to autoxidize, the carotene