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**CONTRIBUTIONS OF AMINO ACIDS AND SUGARS TO COLOR
DEVELOPMENT IN POTATO CHIPS MADE FROM SELECTED POTATO
CULTIVARS**

By

Vanee Chonhenchob

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ABSTRACT

CONTRIBUTIONS OF AMINO ACIDS AND SUGARS TO COLOR DEVELOPMENT IN POTATO CHIPS MADE FROM SELECTED POTATO CULTIVARS

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It has been shown that information on sugar alone may not be used to regularly predict the final color of potato chips. Since Maillard reaction is responsible for the color development in potato chips, this study was aimed at determining the effect of specific amino acids and sugars on chip color. In the first phase of study, model systems were developed to investigate the effect of specific amino acids and sugars on color development in potato chips. Filter paper disks impregnated with 9 selected amino acids in combination with fructose, glucose, and sucrose were fried in vegetable oil at 180°C for 2 min. Lysine, glycine, and tyrosine produced the most intense color, and arginine, aspartic acid, and glutamic acid produced the least. Color development of glucose and fructose systems was not significantly different, but sucrose produced only slight color. Model systems utilizing slices infiltrated with selected amino acids, and glucose suggested that amino

acid-sugar ratio had a significant effect on chip color. Color production was more intense at amino acid-sugar ratio of 10:1 than that of 5:1, 2:1, and 1:1, respectively. In the second phase of study, Cultivars and selections, Atlantic, Mainstay, Shepody, Snowden, and Superior, harvested in 1995 and 1996, and Snowden2, ND2417-6, ND2471-8, NDA2031, and NDO1496, harvested in 1996, were investigated in terms of sugar, free amino acid, and free amino group contents, and chipping performances. In general, good chipping cultivars (Snowden and Atlantic) contained low amounts of glucose, free amino acids, and free amino groups. A poor chipping cultivar (Mainstay) containing high amount of glucose, produced dark chips, regardless of free amino acid and free amino group contents. All selections contained low amounts of glucose, and produced acceptable chips, except ND2471-8. Type of amino acids seemed to involve in chip color formation, corresponding to the model system studies. Statistical results showed that chip color prediction can be improved by combining free amino acid and free amino group contents with sugar content. Free amino group content appeared to be a better predictor for chip color than free amino acid and sucrose contents.

In memory of my parents, Dr. Athorn and Mrs. Pornratana
Chonhenchob whose love and support inspire me beyond words.

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INTRODUCTION

Browning or darkening of potato chips has received extensive study because consumers usually equate light colored potato chips with good quality. The dark color formed under frying conditions is due to the Maillard reaction involving the interaction between reducing sugars and amino acids at high temperatures (Habib and Brown, 1956). Potato tubers stored at temperatures below 7°C have been shown to accumulate reducing sugars, sometimes referred to as low temperature sweetening (Marquez and Anon, 1986). Previous studies have focused on the effect of sugar (reducing and non-reducing) content in potato tubers at harvest or during storage and its relationship to chipping qualities of potatoes (Marquez and Anon, 1986; Roe et al., 1990, 1991). Reducing sugar content in the tuber has normally been used to predict the fry color of potato chips since sugars are generally considered to be the limiting factor in color development in potato chips. Potato tubers containing high reducing sugar content usually process into dark colored chips. However, it has

been shown that information on sugar alone may not be used to regularly predict the final fry color of chips. The variation in the chip color has been ascribed to the free amino acid content present in the tuber (Roe and Faulks, 1991). Very few studies have been aimed at determining the effect of amino compounds on the formation of potato chip color. As the complexities of potato chip color development remain in question, more in depth studies are needed to further elucidate the role of amino acid in the quality of processed potatoes.

LITERATURE REVIEW

The potato (*Solanum tuberosum* L.) is a significant food in many parts of the world (Talbert, 1987). Approximately 62% of the total U.S. potato production have been utilized in processed products (National Potato Council, 1993). Potato chips are one of the major processed potato products. Approximately 12% of the U.S. potato crop are utilized for chip processing (National Council, 1993). Color is one of the most critical quality attributes in the chip processing industry. Chip color is influenced by various factors including cultivar, maturity, handling and storage conditions (Smith, 1987).

It is well established that the color of fried potatoes is due to the Maillard browning reaction involving the interaction between reducing sugars and amino acids at high temperatures (Habib and Brown, 1957). The Maillard reaction will be discussed in greater detail later in this chapter.

Color development in potato chips

A number of studies have shown various factors accounting for color development of fried potatoes. Previous investigators have attempted to correlate the chemical composition in stored potatoes with the chip color. Sweetman (1930) found that an increase in the total sugar content of the tubers stored at temperatures favoring sugar accumulation corresponded to an increase in chip color. Roger et al. (1937) showed that sugar content in the tubers is an important factor in color formation of chips from potatoes stored at various temperatures. Thornton (1940) observed that only reducing sugars, but not sucrose were involved in the dark color developed under frying temperature. Wright and Whiteman (1948) also demonstrated that reducing sugars greatly influence color formation in potato chips. Legault et al. (1945) confirmed that the dark color in potato chips was, at least in part, due to the Maillard reaction. Potatoes containing high sugar content usually processed into unacceptable dark colored-chips (Shallenberger et al., 1959). Recently, Sinha et al. (1992) evaluated different potato cultivars for their chipping potential, sugar content, specific gravity, and yield. The results showed that the correlation between glucose content and chip color was

significant ($r = -0.842$) but the correlation between sucrose content and chip color was not significant ($r = -.070$)

Although reducing sugar content in potato tubers has a major effect on the color of fried potatoes the correlations between reducing sugars and chip color vary considerably. There are factors other than reducing sugars involved in the color formation in potato chips. Fuller and Hughes (1984) studied the effect of sampling from different regions within individual tubers on sugar and color assessment of fried potatoes. They found that the basal region of the tuber contain higher reducing sugars than the apical region. Consequently, they suggested that a sample for sugar analysis should be taken from the basal part of the tuber to be checked for rejection on dark color chip. Sampling appeared to be one of the major factors affecting the variation in chip color prediction.

Although sucrose does not impart darkening of potato chips via the Maillard reaction, sucrose levels in tubers at harvest may play a major role in determining initial rate of reducing sugar accumulation in potato tubers during storage (Sowokinos, 1973). Various studies have investigated the possible role of sucrose in chip color formation. Sowokinos (1978) described a standard sucrose

rating (SR) procedure to rapidly predict chemical maturity at harvest of potatoes for chip processing. Huber and Gould (1979) studied the relationship between sucrose content at harvest and chip color of potato tubers stored at various temperature (5, 7.5, 10, and 12.5°C). They found that potatoes stored at 10 and 12.5°C for up to 6 months generally produced acceptable chips whereas those stored at 5°C for any storage periods (3 or 6 month storage) produced unacceptable chips. Hair and Gould (1979) studied the influence of glucose and sucrose in potato chip discoloration. They also observed the effect of reconditioning time and harvest date on sucrose and glucose concentration. The results showed that reconditioning seemed to be a factor affecting sucrose and glucose reduction in most cases, but was not affected by harvest date. After 1 week of reconditioning, a sharp increase in glucose concentration was found without a concurrent sharp decrease in chip color, indicating that glucose and sucrose are not the only factors, which affect the browning reaction in potato chips. Leszkowiat et al. (1990) utilized filter paper disks immersed in sugars (glucose, fructose, and/or sucrose) and glycine then heated in oil. The results showed that heated filter paper disks saturated

with sucrose and glycine resulted in dark color. They suggested that sucrose participates in the Maillard reaction by thermal hydrolysis which would occur during frying to yield glucose and fructose as previously reported by Shallenberger and Moore (1957) and that hydrolysis of sucrose in the presence of glycine occurred at temperature as low as 150°C. Moreover, they observed that heated filter disks saturated with either reducing sugar or non-reducing sugar resulted in brown color due to caramelization. Caramelization of sugars and Maillard reaction can occur simultaneously. However, Buera et al. (1987) observed that caramelization of sugars has only a slight effect on color development as compared to Maillard reaction.

Shallenberger et al. (1959) simulated frying potato chips utilizing filter paper disks impregnated with solutions of sugars and amino acids. Dark color was observed in the filter paper disks soaked with a solution of sugar and amino acid. They reported that both reducing sugars and sucrose react with amino acids to produce brown color at frying temperatures of potato chips. The observations were consistent between the actual and the model systems. The results showed that chip color was better correlated with reducing sugar content in the tubers

($r = 0.86$), than total sugar ($r = 0.82$). But chip color was poorly correlated with sucrose ($r = 0.39$). However, the best coefficient of 0.983 was observed in multiple correlation between chip color and reducing sugar and sucrose contents in fresh tubers. They proposed the multiple regression equation, which may be used to accurately predict chip color. They also suggested that both reducing sugars and sucrose are significant in determining the suitability of potatoes for chipping.

Marquez and Anon (1986) aimed to accumulate more data on color development during potato frying. They observed that chip color as measured by L (Hunter CDM) increased as reducing sugar content increased. The results confirmed that both reducing sugars and amino acids participated in color development of fried potatoes; fructose yielded the greatest browning followed by glucose. However, they suggested that reducing sugar was the limiting factor in color development since free amino acids did not significantly change with storage conditions.

Even though many studies have been conducted, the limiting factors, which cause variation in the color of the chips, processed from different cultivars remains unclear. Although sugars are the limiting factor in color development (Dahlenberg, 1982; Marquez and Anon, 1986), the

use of sugar level as a predictive test for suitability of processing materials is not always successful. Chip color often varies from what might be expected, based on reducing sugar content. This variation has been ascribed to the differences in free amino acid content in potato tubers (Habib and Brown, 1957; Hope et al., 1960; Roe and Faulks, 1991). Previous studies have shown that the free amino acid pool of potato tubers varied with different levels of nitrogen fertilization (Hoff et al., 1971; Eppendorfer, 1978 and Rexen, 1976). Hughes and Fuller (1984) observed that potato samples containing the same amount of sugar but grown under different levels of nitrogen resulted in different chip color. They reported that increasing nitrogen fertilization lowered the reducing sugar content in potatoes. Increasing nitrogen fertilization was also found to be involved in an increase in free amino acid content (Rexen, 1976). Since free amino acid content in potato tubers is influenced by nitrogen fertilization, Roe et al. (1990) carried out experiments to determine the influence of reducing sugars and amino acid content on fry color of chips grown under different levels of nitrogen fertilizer applications. Potatoes grown under high nitrogen contained lower sugar content, hence, processed into good chips. However, potatoes grown under high

nitrogen had more color per unit of sugar. The results indicated that there seemed to be a synergistic effect between amino acids and sugars in the chip color formation. A year later, Roe and Faulk (1991) determined the role of individual amino acids and sugars in a model frying system utilizing filter paper disks. Color development during frying showed a pattern with 4 distinct phases, corresponding to water content. The phases include: 1) slight but rapid increase in color up to 15 sec due to an effect of oil on the surface of the paper causing the optical characteristic changes; 2) a lag phase, between 15 to 22 sec, which had no color developed due to the high water content of the paper; 3) rapid increase in color after the loss of most water allowing the temperature of the paper to increase, which resulted in a greatly increased rate of reaction and; 4) No further color development with the loss of almost all water between 40 and 120 secs. Various amino acids in combination with glucose, fructose and sucrose were ranked in order of degree of browning. Lysine, γ -aminobutyric acid and glycine were found to elicit the greatest degree of browning in this experiment. No synergistic or depressive effects were reported in the mixed systems using two or more amino acids with glucose. Although different amino acids and sugars

showed different degrees of browning in the model system, Roe and Falulk (1991) stated that the color formed by different amino acids was relatively slight since amino acids are present in excess of sugars. There seemed to be no significant differences between types of amino acid in color formation. Nevertheless, Leszkowiat et al. (1991) investigated the free amino compound, total nitrogen, and dry matter content of tubers in an attempt to correlate these factors with chipping performance of summer potatoes grown in southern Ontario. They reported that the better chipping cultivars generally contained less amino compounds and total nitrogen and more dry matter than the poorer chipping cultivars. They also observed that, in most cases, poor chipping cultivars contained larger percentages of amino compounds, which produced more intense Maillard browning. The results from this study suggested the possible contribution of type and concentration of amino compounds to chipping performance of potatoes.

The Maillard browning reaction

The Maillard reaction is important in many physiological and biochemical processes ranging from the processing of food to diabetes (Talley and Eppley, 1985). Many of its aspects have been widely studied. The Maillard

reaction, a nonenzymatic type of browning, involves the interaction initiated between an amino group of amino compounds including amino acids, amines and proteins, and an α -hydroxy carbonyl group of a reducing sugar and other aldehydes and ketones (Townsend and Hope, 1960; Yaylayan, 1997). The Maillard reaction occurs during food processing and storage and is one of the most important routes to nutritional damage of food proteins (Hurrell, 1984). In addition, the Maillard reaction is primarily responsible for the development of aroma and color in food products (Ames, 1992). Some of these changes may be very desirable as in roasting of coffee, the baking of breads and cakes, the cooking of meats and the frying of potato chips. The reaction may cause undesirable results as in concentrated or dried foods (deMan, 1980). It also results in the formation of potentially toxic compounds such as imidazoles and beneficial compounds with antioxidant activities (Nursten, 1986; Mottram, 1994). Some of the flavor and colored compounds generated by the Maillard reaction are shown in Figures 1 and 2, respectively (Ames, 1992).

Chemistry of the Maillard reaction

Many studies related to the chemistry of the Maillard reaction have been reviewed since the early 1950s. In

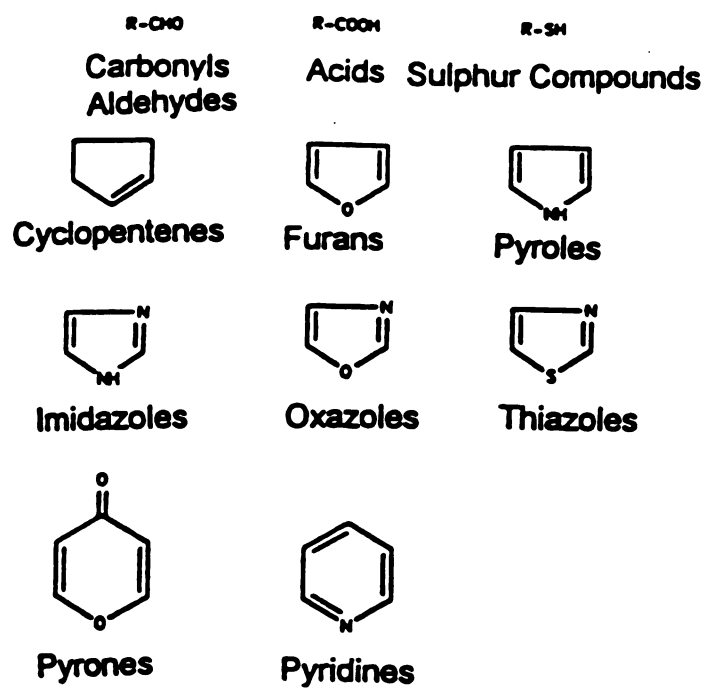


Figure 1. Some aroma componets formed by the Maillard reaction (Ames, 1992).

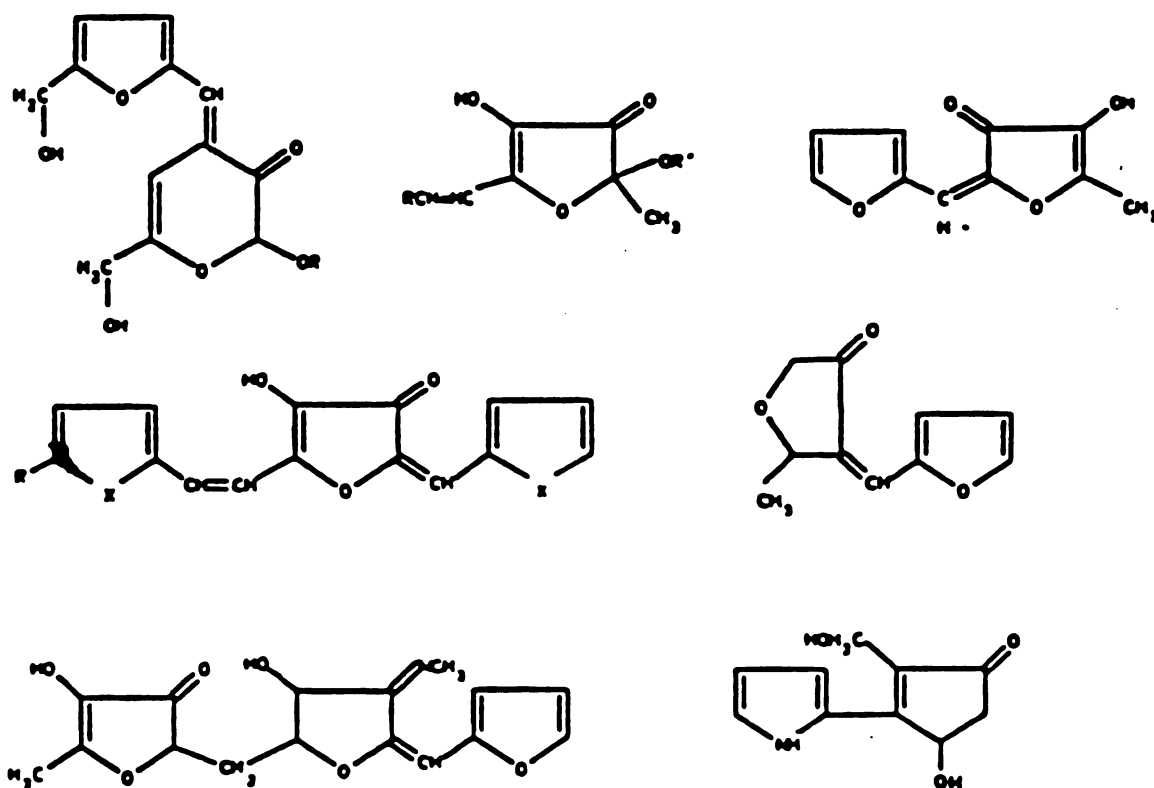


Figure 2. Some colored compounds formed by the Maillard reaction (Ames, 1992).

1953, Hodge suggested the scheme for the Maillard reaction. An outline of the Maillard reaction modified by Ames (1990) from Hodge (1953) and Nursten (1990) is shown in Figure 3. The chemical reaction can be divided into three main stages as follows:

1. The early stage: the formation and degradation of the N-substituted glycosylamine to the rearrangement product of fission products.
2. The advanced stage: the degradation of the rearrangement product, and secondary reactions.
3. The final stage: the production of brown polymers and co-polymers (the melanoidins).

Early Stage

The first step in the Maillard reaction is the addition of a carbonyl group of sugar to an unprotonated amino group resulting in an addition compound. Subsequently the Schiff base is formed with the elimination of water. N-substituted glycosylamine is later formed as a result of cyclisation (Hodge, 1953). This compound readily undergoes further reactions (Figure 3 step A and Figure 4). When the sugar is an aldose, the N-substituted aldosylamine formed undergoes an acid-catalyzed rearrangement to yield the 1-amino-1-deoxy-2-ketose or Amadori Rearrangement

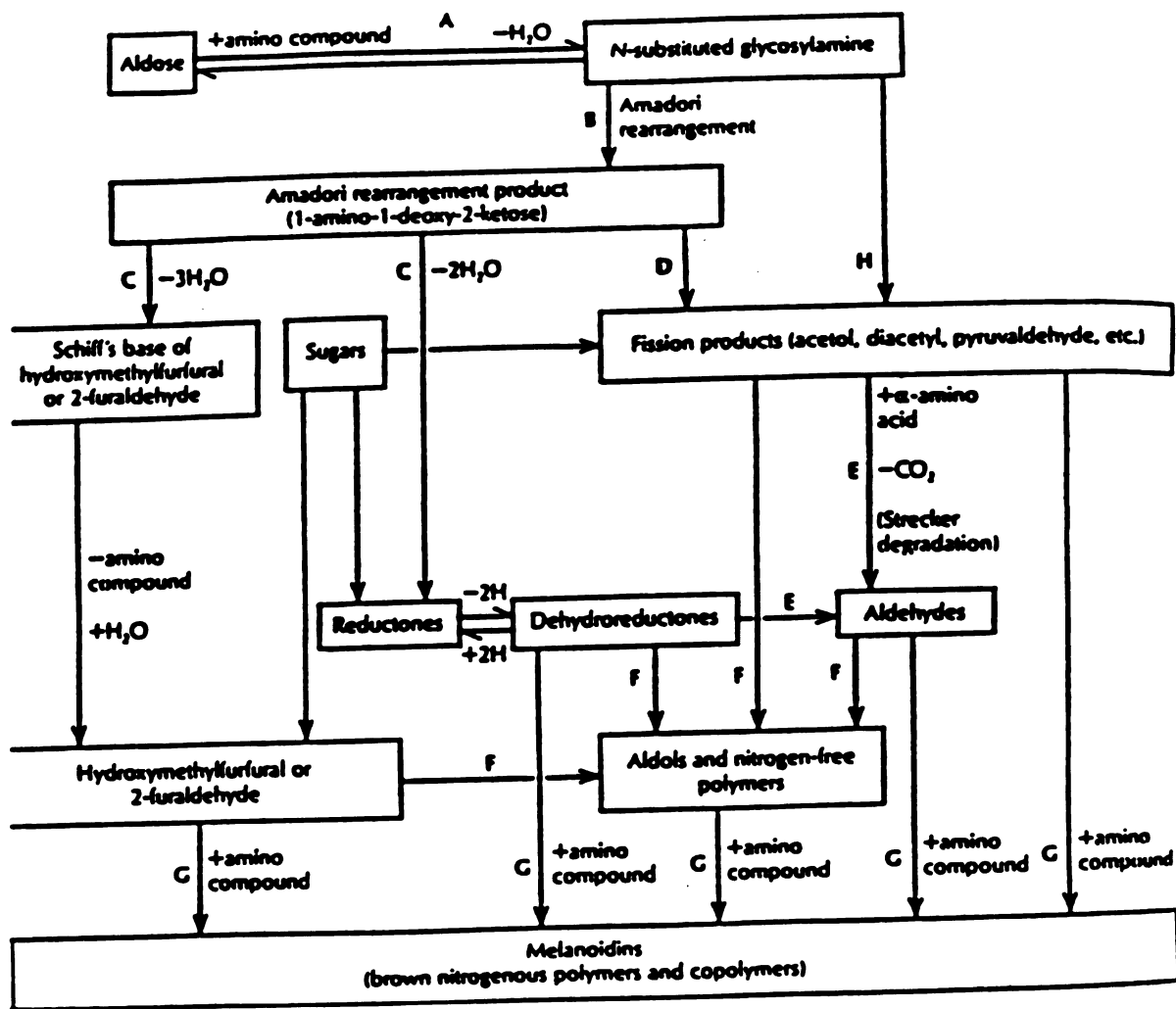


Figure 3. An outline of the Maillard reaction (Ames, 1992).

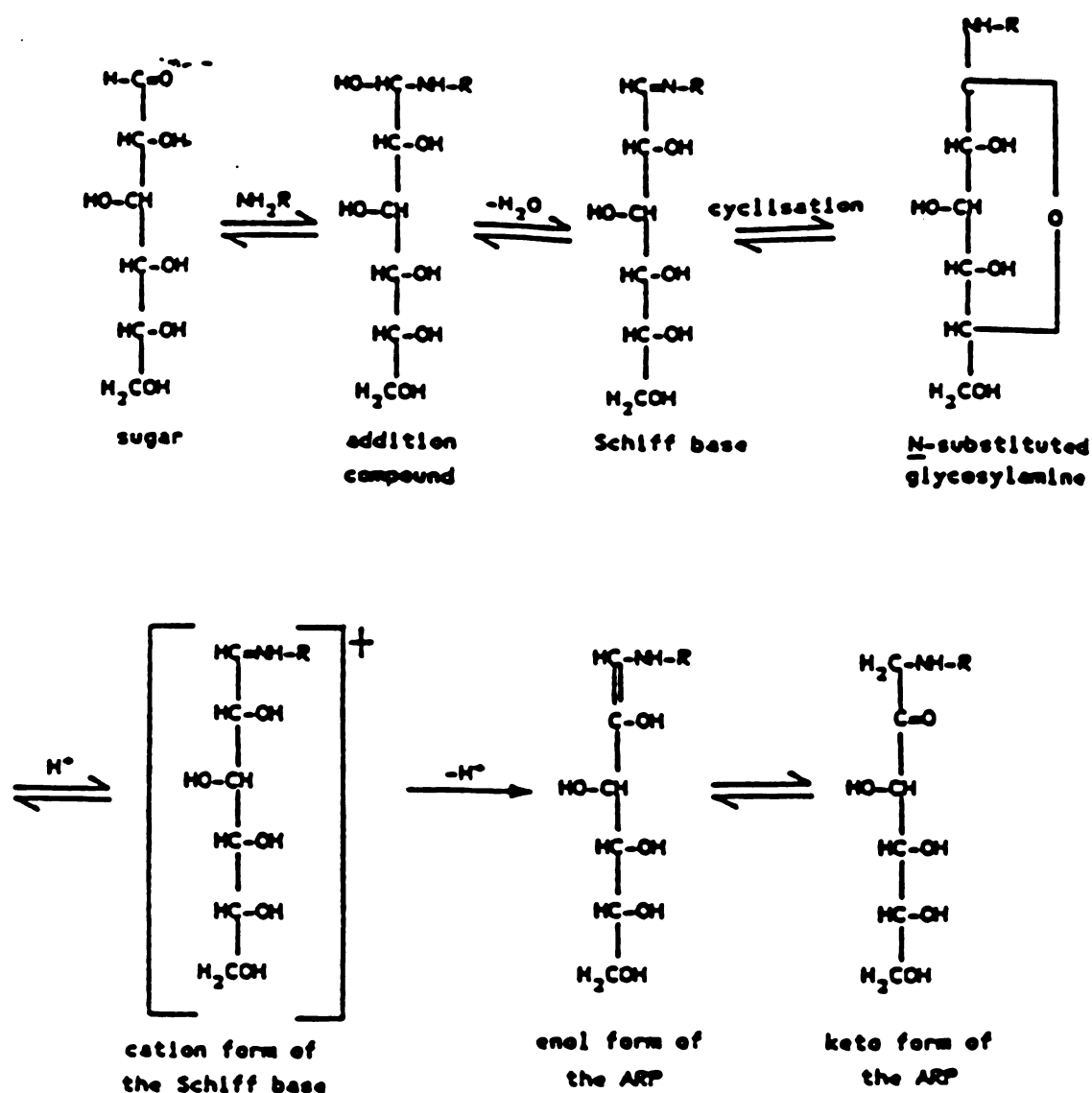


Figure 4. Formation of a 1-amino-1-deoxy-2-ketose (Amadori Rearrangement Product, ARP) from a hexose and an amino compound (Hodge, 1953)

Product (ARP) as shown in Figure 3, step B). According to Namiki et al. (1988), free radicals can also be generated from the glycosylamine without formation of the ARP.

Advanced Stage

The degradation of the Amadori Rearrangement Product consists of following possible pathways:

1) 3-Deoxyosone Route

The formation of 3-deoxyosones from the ARP via 1,2-enolisation results in the formation of 5-hydroxymethylfurfural (HMF) from hexose or furfural from pentose, respectively (Figure 3, step C).

2) 1-Deoxyosone Route

1-Deoxyosones are generated from the ARP via 2,3-enolisation leading to the production of reductones after the elimination of water. The 1-deoxyosone route can also result in pyranone derivatives through the cyclic hemiacetal form of 1-deoxyosone.

3) 1-Amino-1,4-Dideoxysone Route (Figure 3, step D)

Beck et al. (1990) showed that ARPs can degrade to 1-amino-1,4-dideoxysones. These compounds degrade to furan derivatives which are able to undergo a number of condensation and rearrangement reactions.

4) 4-Deoxyosone Route

Although it has not been proved that the formation of 4-deoxyosone route occurs during the Maillard reaction, certain products such as pyrrole, pyridiniumbetaine, and furan have been identified which likely are produced via this route.

5) Fission and Strecker Degradation

It has been shown that ARPs may undergo oxidative degradation to produce carboxymethylamines and C₃ imines. Fission represents step D in Figure 3. As shown in Figure 3, step E, the α -dicarbonyls produced by retroaldolisation and fission reactions can then take part in the Strecker degradation of amino acids resulting in the formation of Strecker aldehydes, aminoenols and carbon dioxide. The Strecker degradation of amino acids is shown in Figure 5.

Final Stage

The final stage of the Maillard reaction is characterized by the formation of melanoidins (Figures 1-3, step G). Melanoidins are high molecular weight, unsaturated, brown nitrogenous polymers and copolymers. However, the chemical structures of melanoidins and the final steps leading to their formation remain undefined.

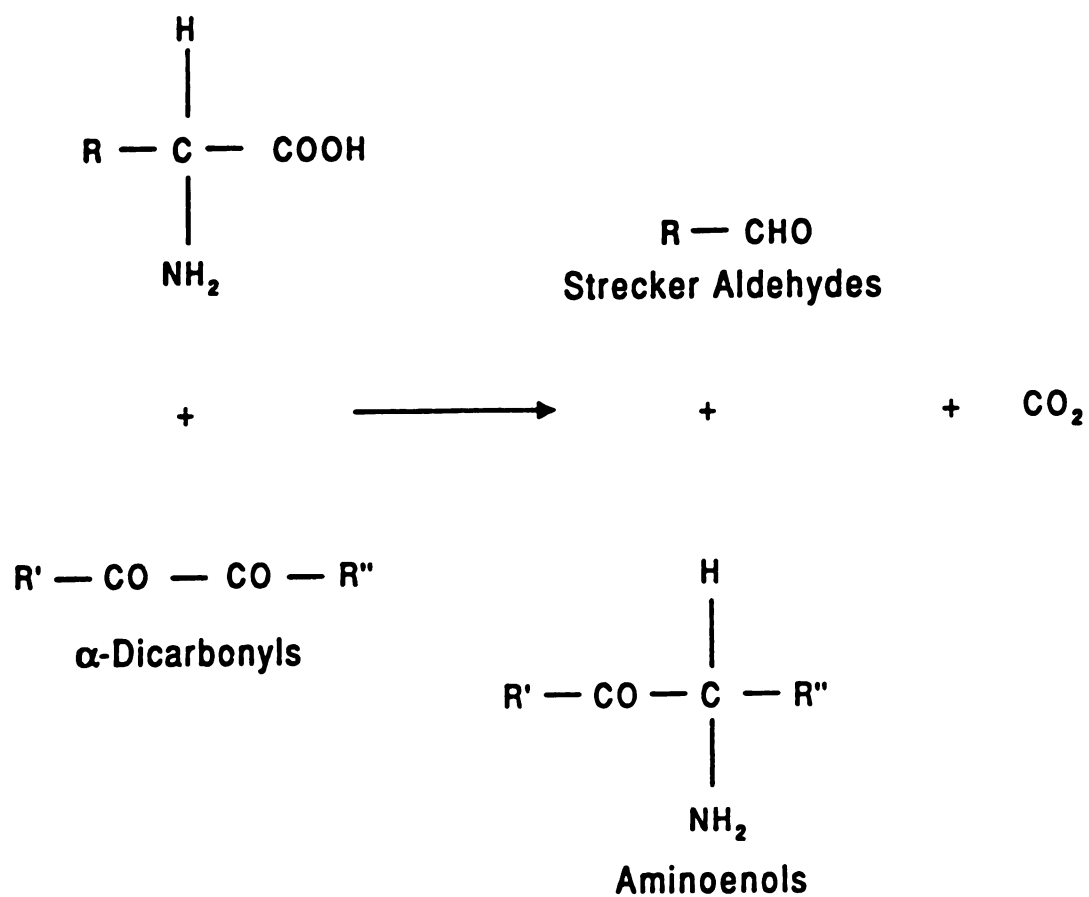


Figure 5. The Strecker degradation of amino acids (Ames, 1992).

A number of studies have described the model systems carrying out the Maillard reaction. Talley and Porter (1968) combined the techniques of previous studies (Ingles and Reynolds, 1958; Shallenberger et al., 1959) and carried out the study to monitor the Maillard reaction. Filter paper disks were treated with solutions of amino acids and sugars and fried in fat to simulate potato chip frying. The results confirmed that amino acids react with sugars to form intermediate compounds, which increased to a maximum value and then decreased. The available amino acids were decreased as the reaction proceeded. Synthesis and loss of intermediates in the reaction may occur simultaneously, therefore, concentration of the intermediates varied as the reaction progressed. Later in 1985, Talley and Eppley used the model system to study the first stage of the Maillard reaction. The intermediates and unreacted amino acids were separated and monitored on an amino acid analyzer. Results showed that types and relative concentrations of amino acids and sugars influenced the rate of intermediate formation.

Nonenzymatic browning in foods is affected by various factors. It has been reported that the type of amino compounds and reducing sugars and the pH of the medium are the factors of primary importance. Since previous

investigators studied the Maillard reaction at different conditions, the results were contradictory in many cases. Ashoor and Zent (1984) studied the effect of amino acid type, sugars and pH on the Maillard browning intensity under identical conditions. Various amino compounds and sugars were compared according to the degree of browning formed under identical conditions. Lysine, glycine, tryptophan and tyrosine were classified into a high browning group. The results showed that the degree of browning increased as the pH of the solutions increased, in accordance with previous reports (Schroeder et al., 1955; Underwood et al., 1959; Pomeranz et al., 1962; Kato et al., 1969; Wolfrom et al., 1974). The browning was first detected at pH 6, reached the maximum value at about pH 10 and then decreased at higher pH.

Water activity has also been shown to be one of the factors influencing the Maillard browning. A maximum browning reaction occurs over the range of water activities (a_w) between 0.3 to 0.7 in most foods (Eichner and Karel, 1972). Eichner and Karel (1972) studied the effect of water content and water activity on the Maillard reaction in the model systems containing varying amounts of water, glycerol, and hydrophilic compounds. They observed that as the water content in the systems increased, the rate of the

browning reaction decreased except in systems containing high viscosity solutions at low water activities. However, the effect of water was complex and depends on various factors, such as the presence of other substances in the systems.

Sugars in potatoes

In plants, sugars are largely produced by photosynthesis and are the major source of carbon and energy for respiration. Previous studies reported that glucose, fructose, and sucrose are the primary sugars in potatoes and are present in approximately equal amount. Other sugars including maltose, xylose, raffinose, melibiose, heptulose, melezitose, and sugar phosphates are present in trace amounts (Talbert et al., 1987). Several non-sugar components such as tyrosine, ascorbic acid, cysteine, glutathione, and inositol present in potato extracts could conceivably react as reducing sugars (Schwimmer et al., 1954). Glucose and fructose, which are reducing sugars, are involved in the browning reaction in processed potatoes. Sucrose, translocated from the leaves to the tubers, is the primary free sugar in potatoes and especially in immature tubers (Sowokinos, 1978). In immature tubers, the rate of translocation is higher than

the rate of metabolism. Hence, immature potatoes contain greater amounts of sucrose than mature potatoes (Sowokinos, 1973). Sucrose plays a major role in tuber development and starch synthesis (Sowokinos and Preston, 1988). The accumulation of sucrose in tuber during growth differs among cultivars. Nelson and Sowokinos (1983) reported that the concentration of sucrose in immature tubers of six different cultivars ranged from 4 to 12 mg sucrose/g fresh weight basis.

Starch is mainly formed from glucose, fructose, and sucrose. The major composition of starch is amylose (25%) and amylopectin (75-79%). Both starch and sugars play an important role during tuber development and storage of potatoes. Major processes during tuber formation and during storage of potatoes are starch biosynthesis and degradation, respectively (Van Es and Hartmans, 1987). During tuberization in potatoes, starch starts accumulating in the sub-apical region of the stolon as found by the shift in carbohydrate metabolism. Sucrose is transported through the stem to the tuber where starch is formed. Hence, sucrose from the cytoplasm, or cell sap is broken down by sucrose synthetase into glucose and fructose, followed by the formation of starch. Starch formation during tuberization is dependent upon equilibria between

the concentration of sugars in the cell sap and the amount of starch formed in the starch granules. The concentration of sugars in equilibrium with starch is greatly affected by cultivar. The permeability of the amyloplast membrane is an important parameter for this entire process (Van Es and Hartmans, 1987).

Starch synthesis and degradation

The metabolic pathways of starch synthesis and degradation presented by Van Es and Hartmans (1987) are shown in Figures 6 and 7, respectively. It is believed that starch synthetase is the major enzyme responsible for starch synthesis during tuber development. Starch synthetases are either bound to the starch granule or soluble in the cytoplasm (Duffus, 1984). In starch synthesis, glycolysis is involved in the degradation of hexose phosphates to dihydroxyacetone-phosphate (DHAP). After DHAP passes through the amyloplast membrane, it is converted to the starch granule via gluconeogenesis. During tuber development, sucrose synthetase actively catalyses the hydrolysis of sucrose to glucose and fructose (Van Es and Hartmans, 1987) while invertase is inhibited (Pressey, 1966). CO_2 , H_2O and energy (i.e., ATP) are generated from carbons in sucrose molecule via oxidation

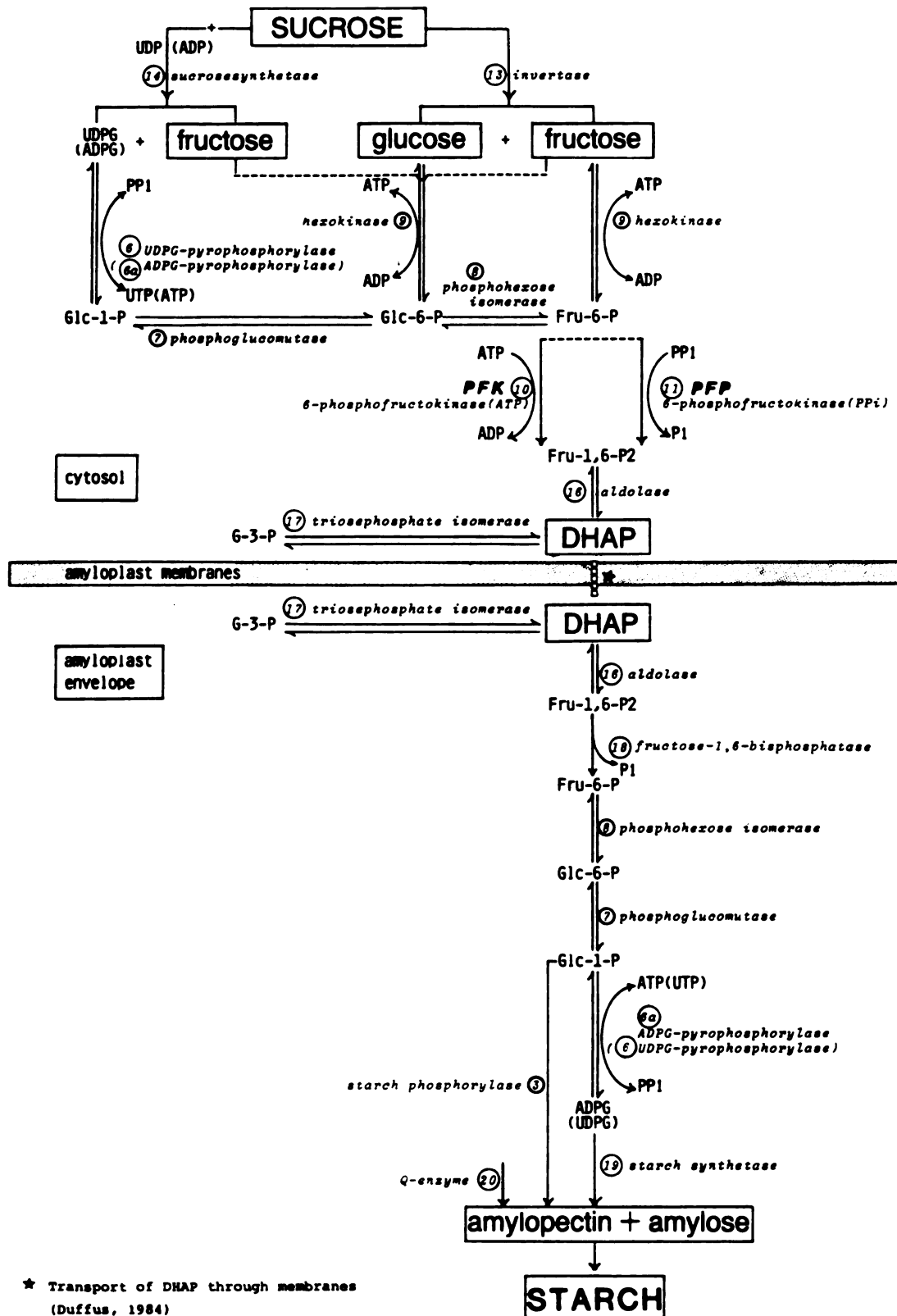


Figure 6. Metabolic pathway of starch in potato tubers during storage (Van Es and Hartmans, 1987).

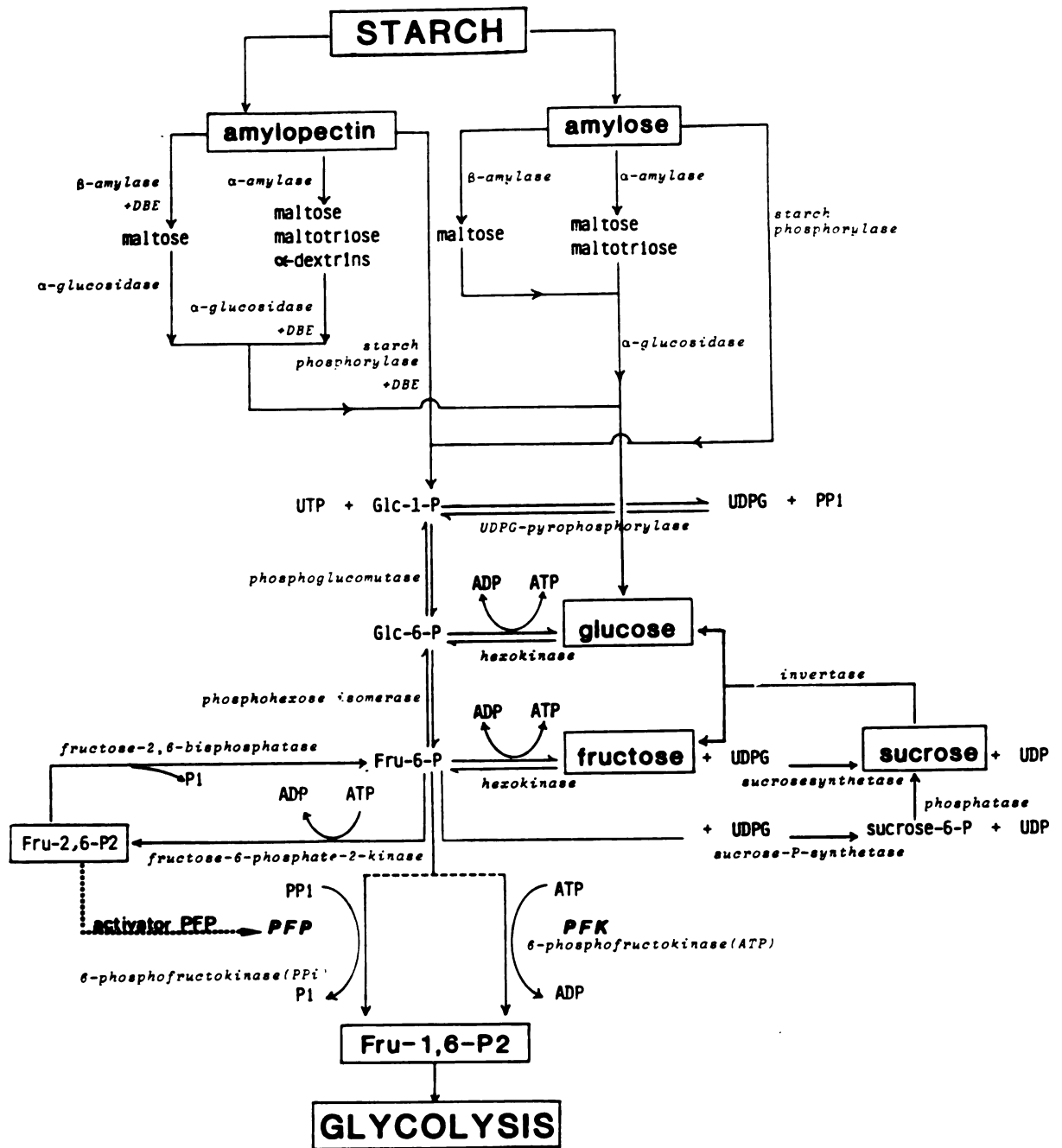
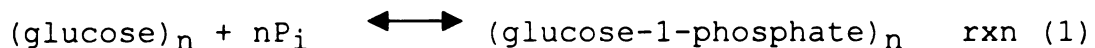


Figure 7. Metabolic pathway of breakdown of starch in potato tubers during storage (Van Es and Hartmans, 1987).

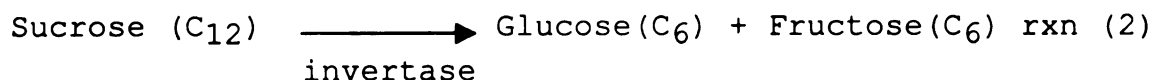
(Mares et al., 1985). Morrell and ap Rees (1985) also studied the sugar metabolism in developing tubers. They measured the content of sucrose, fructose, UDP-glucose and fructose-2,6-bisphosphate and the maximum catalytic activities of various enzymes during tuber development. The results suggested that sucrose is metabolized via UDP-glucose to structural polysaccharides by sucrose synthase. The sucrose is converted to glucose phosphate by UDP-glucose pyrophosphorylase using pyrophosphate generated by PFK (PPi). They suggested that sucrose synthase rather than invertase plays a major role in sucrose breakdown.

At present, it is believed that phosphorylase enzyme plays a major role in starch degradation during storage of potatoes. Phosphorylase catalyses the conversion of glucose into glucose-1-phosphate and vice versa as shown in reaction 1 (Van Es and Hartmans, 1987):



The amyloplast membrane must disintegrate to permit phosphorylase to pass through and catalyze the starch degradation (Van Es and Hartmans, 1987). In addition to phosphorylase, α - and β -amylase enzymes are involved in the degradation of amylose and amylopectin, although to a

lesser extent. Besides amylases, the debranching enzyme hydrolyzes the α -(1,6) glucosidic linkage present in amylopectin (Manners, 1974). During storage, invertase becomes more active than during tuber development. Glucose and fructose are generated via the invertase reaction shown in reaction 2 from the available sucrose pool (Sowokinos and Preston, 1988).



Factors affecting sugar content in potatoes

Previous studies have shown that various factors influence sugar content in tubers. These factors include cultivar, stress during growth, maturity at harvest, specific gravity, location, storage temperatures and storage conditions (Burton, 1969; Iritani and Weller, 1977). The effects of cultivar, maturity, and storage temperature are discussed in greater detail below:

Cultivar

Sugar content varies greatly among potato cultivars during tuberization, at harvest, and during storage (Sinha et. al, 1992). Various cultivars have been investigated at harvest and during storage for their sugar content and

chipping potential (Sowokinos, 1978; Mazza et al., 1983; Nelson and Sowokinos, 1983; Santerre et al., 1986; Sinha et al., 1992). Van Vliet and Schriemer (1960) studied 12 different cultivars grown under identical conditions to determine the effect of cultivars on sugar content of potatoes. Among cultivars stored at 2°C, the differences in maximum reducing sugar levels of potato ranged from 5.9 to 26.5 mg/g fresh weight and the sucrose content ranged from 4.3 to 14.9 mg/g fresh weight. The results were consistent with data collected over a period of 2 years in terms of the order of sugar content. Santerre et al. (1986) investigated the effect of cultivar, harvest date and soil nitrogen on sucrose content, specific gravity and storage stability of different potato cultivars grown in Michigan. This study used sucrose rating (SR) values as a predictor of storage stability and also a method for determining harvest maturity. Significant differences in SR from the interactive effects of harvest-date x variety were observed in both years (1980 and 1981). The differences were due to a variation in developmental rates among cultivars. Recently, Sinha et al. (1992) determined the effects of varieties, date of harvest, and year of production on chipping performance, sugar levels, specific gravity and yield of selected potato cultivars grown in Michigan. In

this study, variety and year of production showed a significant effect on glucose content and chip color. They also reported that variety, date of harvest and year of production had significant effect ($p < 0.01$) on yield. Iritani and Weller (1977) elucidated the relationship between sucrose and reducing sugars of two different cultivars, Russet Burbank and Kennebec, during growth, after storage and after 3 week reconditioning at 15.6°C (60°F). The significant differences in sugar alteration in response to low and high temperature storage and reconditioning were found between cultivars. The sucrose content was at a minimum level in later harvested tubers of both cultivars. Nelson and Sowokinos (1983) compared three new cultivars (Crystal, Dakchip, and Lemhi) with processing cultivars (Kennebec, Norchip, and Russet Burbank) in terms of yield, chipping quality and sucrose content at various harvest date. Norchip showed the best chipping color as compared to others at any harvest date. Relationships between tuber sucrose and chipping performance were also investigated. They found that tuber sucrose was better correlated with chip color in cultivars from early to midseason than later in the season. Mazza et al. (1983) also reported the changes in sucrose content of Kennebec, Russet Burbank, and Norchip during growth and storage as

influenced by cultivars. The study was aimed at elucidating the relationships between sucrose, reducing sugar, ascorbic acid, protein, and dry matter, with the color of fried potatoes. They concluded that the relative importance of each parameter varied with cultivars. Previous studies have also observed that a decrease in sucrose content in tubers to specific values prior to harvest is influenced by cultivar (Sowokinos, 1973; Nelson and Sowokinos, 1983). Some cultivars such as Lemhi and Crystal maintain high sucrose levels at physical maturity. But other cultivars, including Norchip, Dakchip, Kennebec and Russet Burbank, have potential to decrease the sucrose levels to desirable values prior to post harvest storage (Sowokinos, 1988).

Maturity

The state of maturity prior to harvest is an important factor in storage performance and processing quality of potatoes (Sowokinos, 1983; Herrman et al., 1995). In certain cultivars, tubers at maturity contain only trace amounts of sugars (Talbert et al., 1987). Immature tubers contain higher percentage of free sugars and low percentage of starch (Samotus and Schwimmer, 1962). Sucrose is a primary free sugar in immature potatoes (Sowokinos, 1978).

Sowokinos (1973) compared the physiological and compositional characteristics between good and poor potato processing cultivars at maturation. At similar states of maturity, good and poor processing varieties did not show differences in tuber development, starch, reducing sugar, and soluble protein contents, and sucrose synthetase cleavage activity. Nevertheless, as maturity was reached, good processing varieties accumulated less sucrose and had higher rates of sucrose reduction as compared to poor processing varieties.

Determination of maturity

The precise definition of maturity remains unclear, whether it is sufficient to correlate physical maturity with physiological maturity where tubers contain minimum sugar content. Physical maturity is defined by vine senescence, tuber yield, and the degree of skin set or periderm adherence (Iritani and Weller, 1980). Sowokinos and Preston (1988) described a rapid technique to monitor the chemical maturity of potatoes in the field, at harvest, and in storage based on the combination of sucrose and glucose content of tubers and a standard test of chip color. They suggested a series of management steps to minimize the detrimental effects of reducing sugars on

quality of final potato processed products by using the chemical maturity monitoring (CMM). This method has been commercially used in potato industry for more than 15 years and can be beneficial for storage management of immature and/or under stress processing potatoes. Stresses can occur during maturation in the field due to the effect of moisture, heat, cold, etc., or during and after harvest from handling, cold, high CO₂, excessive heat, aging, etc. (Sowokinos et al., 1987). Sucrose and glucose contents present in tubers are measured by using a Yellow Springs Instrument (YSI) industrial analyzer, model #27 (Sowokinos et al., 1985). Sowokinos and Preston (1988) proposed the sucrose rating (SR = mg sucrose/g tuber) for excellent chipping cultivars at 1.5 or below. However, this specific value varies among cultivars. Typically, the safe values for sucrose rating and percent glucose on a fresh weight basis for Norchip potatoes in stress-free storage are less than 1 and 0.035, respectively. The safe values for other processing cultivars should be close to those suggested for Norchip in 10°C (50°F) stress-free storage. Higher concentrations of sucrose and glucose than the safe values indicates a demand for storage condition improvement. Color of chip is determined based on the scale of 1 (lightest) to 5 (darkest) according to the standard chip

color chart developed by the Potato Chip/Snack Food Association. Chips with color of 1 and 2 are in an acceptable range.

Recently, Herrman et al. (1995) studied the relationship between physical and physiological maturity components and processing performance of potato stored for 13 months. Three different cultivars were grown under three levels of nitrogen fertilizer. For all treatment combinations, potatoes were physiologically mature for processing as sucrose content was less than 1.5 mg/g fresh weight) at harvest but the potatoes were different in terms of physical maturity during tuber growth and at harvest. A quadratic regression model was used to predict the optimal processing date in which the lightest chip color was predicted. The optimal processing dates for less physically mature potatoes; Russet Burbank and Gemchip were later in the storage season. The results suggested that physical/physiological maturity data taken shortly prior or at harvest may be helpful when combined with chemical maturity data in selecting processing potatoes for long term storage.

Storage temperature

Most potato chip processors rely upon potatoes from storage, therefore the role of stored potatoes is particularly important in the potato chip industry. The accumulation of sugars in potato tubers stored under low temperature has been widely studied. In general, storage of most processing potato tubers at temperature below 10°C results in sugar accumulation known as low-temperature sweetening (Burton and Wilson, 1978). This cold sweetening process increases rapidly at temperatures below 6°C (Van Es and Hartmans, 1987). Isherwood (1973) found that the increase of sugar content was higher than 2% when potatoes were stored at 2°C. However, storage at high temperature has been shown to result in excessive weight losses, rotting and sprouting (Hair and Gould, 1979). Therefore, storage conditions must be optimized for high and low temperature conditions. Processing potatoes are normally stored at 10°C for a short period after harvest, or at 7-8°C, after initial wound healing at a higher temperature for prolonged storage period (Burton and Wilson, 1978).

A number of studies have investigated the effect of storage temperature on sugar content of various stored potato cultivars. Many studies have been aimed at

selecting the optimum storage conditions to provide quality potatoes for processing. Under identical conditions, cultivars differ in their response to storage conditions in such things as the potential for accumulating sucrose and reducing sugars. It has been previously reported that sucrose content of potatoes was higher at storage temperatures of 5°C than at 7 or 8.2°C (Iritani and Weller, 1977); Schwimmer et al., 1954; Clegg and Chapman, 1962; Burton 1969; 1974). Hyde and Morrison (1964) investigated the influence of storage temperature on reducing sugars, pH, and phosphorylase enzyme activity and the effect of these factors on chipping quality. The increase in phosphorylase activity and reducing sugars in tubers stored at 4.4°C (40°F) indicated that low temperature is involved in sugar accumulation and chip quality. Samotus and Schwimmer (1962) reported the loss of sucrose and the increase of reducing sugars in potatoes stored at 25°C. They also reported that the accumulation of fructose was more predominant in immature tubers while sucrose accumulation was more prominent in mature tubers, at 0°C storage. Coffin et al. (1987) investigated the effect of low temperature storage (5, 10, and 20°C) on sugar content and chip color of the cultivars, Kennebec and Simcoe, and

the selection, ND 860-2 harvested in 1984 and Norchip, Simcoe, Onaway, and ND 860-2 harvested in 1985. All tubers stored at 5°C showed the largest increases in sugar content. The initial rate of sucrose production at 5°C was much slower than at 0°C storage, which was also reported by Ewing et al. (1981). On the contrary, storage at 20°C resulted in a decrease in sugar content in all samples. The results indicated that low temperature is involved in sugar accumulation.

Isherwood (1973) studied the starch-sugar interconversion and respiration of mature and immature potatoes as a result of a change in storage temperature (from 10°C to 2°C and back to 10°C). The results of this study showed that the increased respiration, which accompanied any change in temperature was related quantitatively to the formation of sucrose from starch (+10° to 2°) and of starch from sugar (+2° to 10°). At low storage temperature, approximately 1 mole of ATP in UTP form was required for 1 mole of sucrose formation. The possible biosynthetic pathways for the starch-sugar interconversion in potatoes during low and high storage temperature suggested by Isherwood (1973) are shown in Figures 8 and 9, respectively. Later in 1976, Isherwood

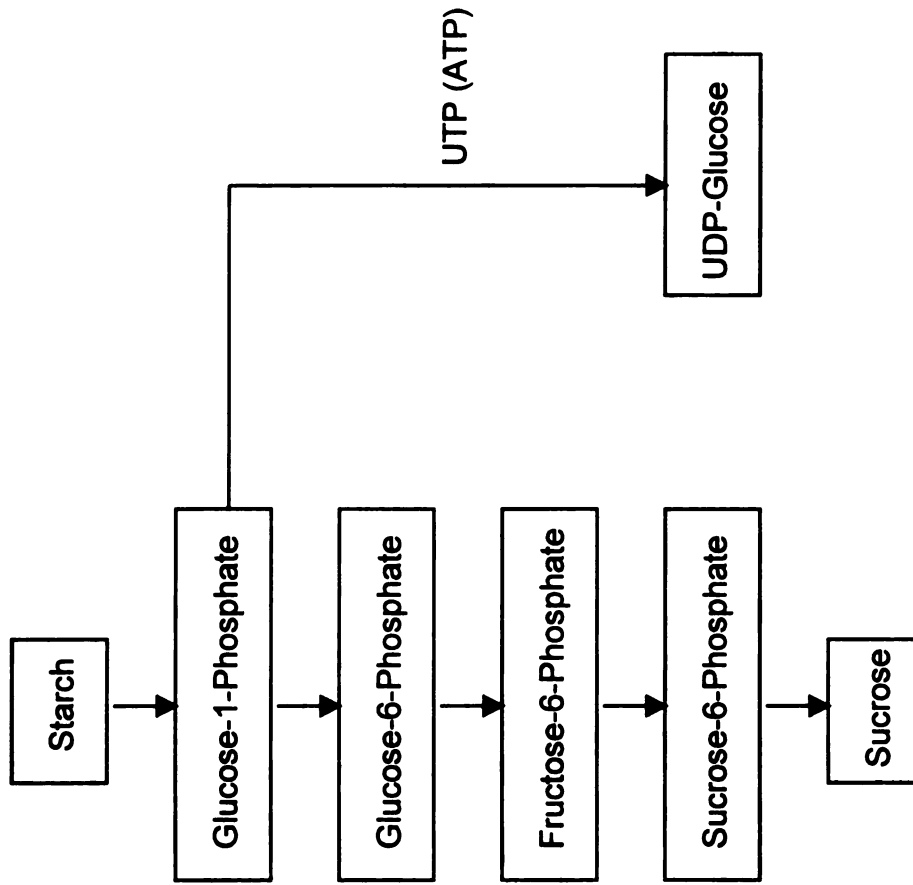


Fig. 8. The biosynthetic pathway of the conversion of starch to sucrose during low temperature storage.

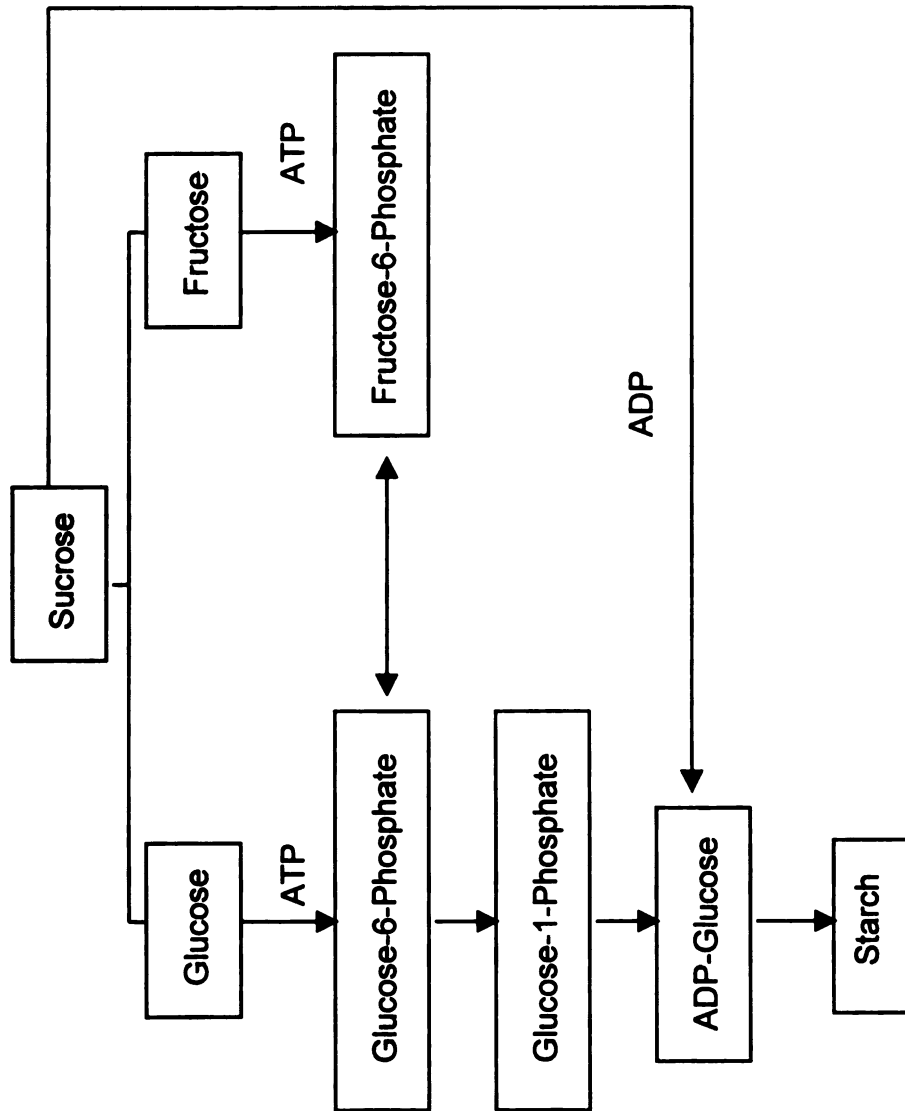


Fig. 9. The biosynthetic pathway of the conversion of sugars to starch during high temperature storage.

particularly studied the steps in the pathways of the interconversion of starch and sugars, which occur during the temperature changes. He followed the changes in the phosphate esters, sugars, and respiration of mature potato tubers (Variety King Edward). The results suggested that the reactions in the tissue occur in two phases. When potatoes were transferred from 10°C to 2°C, the sugar concentration remained fairly constant in the first phase (up to 4 days). In the second phase (after 4 days), sucrose concentration markedly increased. However, a two phase pattern was not so marked in the case of potatoes transferred from 2° to 10°C. The results suggested that the unknown factor involved in controlling the formation of sucrose appeared to be the amyloplast membrane. Temperature changes (raising or lowering) influence the balance between electron transport activated influx and a passive efflux represented by the flow of metabolites between the starch granule in the amyloplast and the cytosol (Kaback and Barnes, 1971). Isherwood (1976) referred to the previous study showing the particular evidence of the effect of temperature on the balance between influx and efflux of metabolites. After long storage at -1°, +1°, and +3°, the maximum accumulation of sugar was 6.7, 3.5 and 1% respectively. This result

indicated that lowering temperature reduces the influx relative to the efflux causing sucrose to accumulate outside the amyloplast. Isherwood (1976) also reported the changes in the amyloplast membrane surrounding the starch grains in potatoes stored at low temperature. Although, electron micrographs indicated that the amyloplast membrane of potatoes stored at 2° for 38 days remained unchanged, the chemical composition was affected by low storage temperature. He suggested that the characteristics of the amyloplast membrane are important in regulating the movement of metabolites through the membrane.

Tishel and Mazelis (1966) compared the activities of several enzymes involved in sugar transformations; phosphohexose isomerase, glucose-6-phosphate dehydrogenase, aldolase, and invertase in potatoes stored at low temperature and at room temperature. The results suggested that low temperature induces an increase in sucrose, invertase activity and reducing sugars, followed by a decrease of phosphohexose isomerase activity. Several investigators studied sugar accumulation at low temperature accompanied by a change in invertase activity in potatoes. Pressey and Shaw (1966) suggested that low storage temperature results in a rapid conversion of starch to reducing sugars and a rapid increase in invertase activity.

Morrel and ap Rees (1986) studied the enzyme activities and sugar content of potatoes stored at 5 and 10°C and found that invertase is one of the key enzymes in low temperature sweetening of potatoes.

Sucrose accumulation in potato tubers exposed to high temperature was reported in the previous studies (Yamaguchi et al., 1966; Timm et al., 1968; Verma et al., 1974). Although it is well documented that the reducing sugars increase at lower storage temperatures, the sucrose content appears to be higher at the high storage temperature (7-10°C). The accumulation of sucrose at high temperature (7-18°C) begins when dormancy is broken after long storage time (Van Vliet and Schriemer, 1963). Clegg and Chapman (1962) observed that potato chip color may be adversely affected by high temperature. Increased permeability of the amyloplast membrane accompanied by increased sugar content in potatoes stored at 40°C was previously reported by Nielsen and Todd (1946). In 1966, Yamaguchi et al. studied the effect of high temperature exposure on sugar conversion and chip quality of White Rose and Kennebec variety potatoes. They observed that sucrose content in both varieties decreased with time when stored at 25°C or lower. At 30°C, sucrose content in the tubers had no

change or increased slightly. Sucrose content markedly increased after 2 week-storage at 33°C in both varieties. These tubers produced darker colored chips than those stored at lower temperature. The results were confirmed by Timm et al. (1968) who also reported that the reducing sugar content was not altered after 2 weeks of storage at 20 or 33°C. Later in 1974, Verma et al. confirmed the findings of previous studies by investigating the increase in total sugar content due to the increase in sucrose when potato tubers were kept at high storage temperature in a farm store in India (temperature between 24.7 and 36.2). However, they observed that high storage temperature holding for 4-5 weeks did not adversely affect the chip quality.

Amino compounds in potatoes

In potato tubers, nitrogen occurs primarily in the form of proteins, non-protein compounds (such as the free amino acids), and inorganic nitrogen (Van Es and Hartmans, 1987). Approximately 60-75% of the total nitrogen in the potato is the non-protein fraction present as free amino compounds (Ashford and Levitt, 1965; Kapoor et al., 1975). Other organic nitrogen components in the potato tuber include the alkaloids, vitamins, purines, pyrimidines,

quaternary ammonium compounds (Talley et al., 1984), soluble nucleotides, and amides (Li and Sayre, 1975). The inorganic nitrogen fraction contains nitrate and nitrite. The free amino acid content and protein composition of potatoes are affected by cultivar, year of cultivation, nutrition, environment, and origin (Talbert et al., 1987; Van Es and Hartmans, 1987).

The degradation of protein to free amino acids in potato tubers during storage has been studied previously (Fitzpatrick and Porter 1966; Brierley et al., 1996). Habib and Brown (1956) reported that there was no change in amino nitrogen of potatoes stored at 4.4°C (40°F), but markedly decreased after reconditioning at 23.9°C (75°F). About the same time these workers observed the effect of reconditioning on the loss of basic amino acids (Habib and Brown, 1957). Fitzpatrick and Porter (1966) studied the changes in sugars and amino acids in fresh, cold stored and reconditioned potatoes and reported that the storage conditions and the length of storage period influence the free amino acid content. They reported an increase of free amino acid nitrogen as a result of protein degradation and a constant level of total nitrogen in potato tubers. They also observed an increase of amino acids on hydrolysis of the potato extracts, but a decrease in the nitrogen

recovered from amino acid analysis. On the contrary, when the chip extracts were hydrolyzed, the results showed an increase in both the amino acids and the nitrogen recovered from the amino acid analysis. More significant increases on hydrolysis occurred in serine, glycine, alanine, and leucine, as they are more reactive with reducing sugar (Ingles and Reynolds, 1958).

Very recently Brierley et al. (1996) studied the factors influencing the free amino acid content of the potato cultivars Pentland Dell and Record stored at 5°C and 10°C up to 40 weeks. They found an increase in free amino acid content, which occurred during the latter part of storage caused by an increase of proteinase activity on the break of dormancy. Protein synthesis and amino acid accumulation were greater at 10°C than at 5°C indicating that rate of amino acid translocation was greater at higher temperature. Proteinase enzyme may be of importance in regulating the free amino acid pool size during storage, as it showed a pronounced substrate specificity for natural tuber proteins including patatin and the 17-25 kDa protein fraction. As a result, such factors as proteinase activity, protein synthesis and overall balance of nitrogen flow, depending on the state of dormancy of the tuber, influence the free amino acid content of stored potatoes.

Therefore, storage duration influences the free amino acid content of potato tubers. Short-term reconditioning showed no effect on altering the free amino acid content as it did not change the net balance of nitrogen flux between free amino acids and proteins. Hence, reconditioning process improves quality of fry potatoes only by lowering the reducing sugar content. Due to the excessive concentrations of free amino acids over total reducing sugars, the color formation on processed potatoes is limited by only the latter. However, in Pentland Dell stored at 10°C, the results showed an increase in fry color as free amino acid content increased, with no increase in reducing sugar content. This result indicated the synergistic effect of free amino acids on fry color supporting the finding of Roe et al. (1990).

Brierley et al. (1996) observed the accumulation of asparagine and glutamine in Pentland Dell stored at 10°C indicating temperature dependence in this cultivar. Both asparagine and glutamine showed a possible synergistic effect on chip color in the case of Pentland Dell tubers stored at 10°C. The results showed an increase between 40 and 162% of these amides during the latter half of storage. No conversion between the two amides was observed

suggesting that both amides play an equally important role in processing quality.

Previous studies reported that increasing the nitrogen content of tubers by fertilizer application affects the proportions of individual amino acids. These include a decrease in the essential amino acids, lysine, leucine, isoleucine, threonine, methionine, tryptophan and cysteine accompanied by an increase in the proportion of aspartic and glutamic acids (Rexen, 1976). Millard (1986) studied the effect of nitrogen application on the nitrogen content and amino acid composition and yields of potato tubers. They observed that nitrogen application increased dry matter production and nitrogen concentration in the potato tubers resulting in an increase in yields of amino acids. Increasing nitrogen concentration of the tuber did not affect the proportion of amino acids. Rexen (1976) stated that the content of particular amino acids in the nitrogen seems to be an important factor in potato chip processing. He suggested that the concentration of tyrosine and proline must be high while that of leucine and isoleucine must be low in order to minimize the color formed via the Maillard reaction.

Objectives

This study was divided into 2 parts; the model system study and the potato storage study. The primary objectives of this study were as follows:

1. To determine the differences between selected good chipping versus poor chipping cultivars in terms of sugar content, free amino acid composition, free amino group content and chipping performance.
2. To determine the effect of specific amino acids and sugars on color development in potato chips based on the model systems.
3. To determine the effect of amino acids and sugars on color development in potato chips made from stored potato tubers.

MODEL SYSTEM STUDIES OF THE MAILLARD REACTION IN POTATO CHIPS

ABSTRACT

Model systems were developed to investigate the effect of amino acids and sugars on color development in potato chips. Filter paper disks impregnated with solutions of 9 selected amino acids in combination with glucose, fructose, and/or sucrose were fried in fresh vegetable oil at 180°C for 2 min. Lysine, glycine, and tyrosine were found to produce the most intense browning. There was no significant difference between fructose-amino acid and glucose-amino acid systems, but sucrose-amino acid system produced only slight color. Different batches of potato slices were vacuum infiltrated with varying concentrations of selected amino acids and glucose. Darker chips were from slices infiltrated with the amino acids-glucose ratios of 10:1, 5:1, 2:1, and 1:1, respectively. Slices infiltrated with lysine-glucose, and leucine-glucose produced unacceptable chips. Slices infiltrated with aspartic acid-glucose produced excellent chip quality.

There did not appear to be any synergistic effect between glycine, and leucine. The effect of aspartic acid was significant in reducing the browning color of chips.

MATERIALS AND METHODS

1. Model systems using filter paper disks

1.1. The model system studies utilized filter paper disks impregnated with solutions of amino acids and sugars in order to determine the effect of individual amino acids and sugars on Maillard browning.

All chemicals used were of analytical grade and obtained from Sigma Chemical Company (St. Louis, MO). Stock solutions (0.05M) of L-isomer amino acids (arginine, aspartic acid, glutamic acid, glycine, isoleucine, leucine, lysine, methionine, and tyrosine) and sugars (D-fructose, D-glucose, and sucrose) were prepared for the study in 0.05M phosphate buffer solutions (pH 6.5). To prepare working solutions, 25 mL of each of the amino acid stock solutions were mixed with 25 mL of each of the sugar stock solutions. All mixtures were adjusted to pH 6.5 with 0.1M HCl or 0.1M NaOH. Hoover (1967) suggested the use of thick papers such as Whatman No. 3MM or a glass fiber paper to simulate potato chips. In this experiment, filter paper disks were prepared by soaking 30 Whatman No. 3MM disks,

5.5 cm diameter, for 30 min in the appropriate solutions. The disks were then air dried and fried in fresh vegetable oil at 180°C for 2 min with stirring in a thermostatically controlled fryer. Each sample was done in duplicate. Filter paper disks impregnated with phosphate buffer were fried as a control. The color of the filter paper disks was evaluated using Agtron E-10 colorimeter (Filper Magnuson, Reno, NV).

1.2. Filter paper disks were also impregnated with potato juices to show the effect of amino acid and sugar naturally present in various cultivars on Maillard browning intensity.

Five potato cultivars, Atlantic, Mainstay, Shepody, Snowden, and Superior were obtained from Michigan State University Montcalm Research Farm in September 1995. Atlantic and Snowden are considered to be good chipping varieties, while the other varieties vary in their chipping ability from moderate to poor. Two hundred grams of tuber tissue were taken from the middle of 8 peeled potatoes and juiced in the Acme juicerator (Model #6001 Acme Juicer Mfg Co., Sierra Madre, CA). The potato juice samples were centrifuged at 3,500 rpm for 20 min. To each tube containing 9 mL phosphate buffer solution (pH 6.5), one mL juice sample was added and the solution was mixed gently.

Filter paper disks were loaded with 1 mL of juice solution with a Hamilton gastight syringe. After air drying, treated filter paper disks were fried in fresh vegetable oil at 180°C for 2 min. Potato chips were also made from each of the tuber varieties according to Gould and Plimton (1985). The color of filter paper disks and potato chips was evaluated using Agtron E-10 colorimeter. The remaining juices were kept frozen for sugar analysis.

2. Model systems using potato slices.

2.1. Potato slices were vacuum infiltrated with varying concentrations of selected amino acids and sugars to determine the effect of relative proportion of selected amino acids on Maillard browning.

In this model study, lysine, leucine, and aspartic acid were selected as a representative of high, intermediate, and low browning groups, respectively (Ashoor and Zent, 1984). Stock solutions (0.1M) of each amino acid and glucose were prepared for the study in 0.1M phosphate buffer (pH 6.5). To obtain the amino acid-glucose molar ratios of 10:1, 5:1, 2:1, and 1:1, varying quantities of each amino acid and glucose were mixed to a final volume of 200 mL. The working solution was adjusted to pH 6.5 with 0.1M HCl or 0.1M NaOH. Potato slices (10 slices for each

solution) of Snowden were vacuum infiltrated with each working solution. The vacuum chamber pressure was maintained at 1×10^3 kPa for 20 min. Potato slices were fried in fresh vegetable oil at 180°C for 2 min. Slices infiltrated with phosphate buffer solution were fried as controls. Each sample was done in duplicate. Similar experiments were performed to determine the synergistic effect between each amino acid tested. The molar ratio of amino acid to glucose was 1:1. Slices infiltrated with each amino acid alone were fried to compare with those infiltrated with the mixture of amino acid and glucose. Slices infiltrated with phosphate buffer were fried as a control. All samples were done in duplicate.

Analytical methods

1. Sugar analysis

The preparation of samples for glucose and sucrose analysis was according to Sowokinos and Preston (1988). A 200 g sample of fresh peeled potato tissue was prepared from the center part of 8 uniform sized tubers. Potato juice was extracted from the prepared samples using an Acme juicerator (Model #6001 Acme juicer Mfg, Co., Sierra Madre, CA). Three 100 mL aliquots of cold, distilled water were passed through the juicerator, allowing one to two minutes

between each wash. The juice sample was mixed and diluted to 430 mL with cold, distilled water. The potato extract was refrigerated for approximately 1 hour before further determination. A 10 mL sample of extract was placed in the vial for analysis by YSI-2700 glucose analyzer (Yellow Springs Instrument Co., Yellow Springs, OH). A 0.5 mL volume of potato extract was injected into the YSI analyzer by an autosampler. The YSI instrument measures the hydrogen peroxide produced from the reaction of glucose with the immobilized glucose oxidase in the system. The hydrogen is oxidized at the platinum anode, producing electrons. The YSI analyzer reports glucose concentration, as it is linearly proportional to the flow of electrons. The analyzer uses a combination of 0.47M of mono and dibasic phosphate buffer ($\text{Na}_2\text{HPO}_4\text{-NaH}_2\text{PO}_4$), pH 8.0. Calibration took place automatically after every five samples. The YSI model 2700 provided glucose and sucrose readings in g/L. All samples were analyzed in duplicate.

Calculation

Glucose and sucrose contents of potato extract samples were calculated according to the following equation:

$$\text{Sugar content (g/g fresh weight)} = \frac{\text{YSI reading (g/L)} \times 0.43\text{L}}{200 \text{ g}}$$

2. Chip Color Measurements

Color development of fried filter paper disks and potato chips were measured using the Agtron process analyzer model M-35-D (Agtron Incorporation, Sparks, NV). Agtron readings were made on the red scale. The Agtron number corresponds to the chip color chart developed by the Potato Chip/Snack Food Association (1 = light chips, 5 = dark chips). Chips with Agtron number less than 45 were considered unacceptable (colors 3 through 5 on chip color chart). Chips with Agtron number greater than 60 were considered excellent (colors of 1 and 2).

3. Statistical Analysis

Single and multiple correlation and regression analyses were performed using SPSS program, version 6.1. The analysis of variance (ANOVA) was performed using Statview computer program.

RESULTS AND DISCUSSION

1. Filter paper disks

1.1 Filter paper disks impregnated with solutions of amino acid and sugar

Amino acids were selected based on those present in greatest amounts in potato tubers (Kaldy and Markakis, 1972). Primary sugars in potato tubers were glucose, fructose, and sucrose. The molar ratio of amino acid and sugar was 1:1 in order to obtain the stoichiometry of the initial stage of the Maillard reaction. The pH of all solution systems was 6.5 corresponding to the average pH of potato juice. The final concentration of amino acid was as low as 0.001 M in order to avoid the low solubility of some amino acids such as L-tryptophan and L-tyrosine (Ashoor and Zent, 1984). Color development of fried filter paper disks impregnated with various amino acid/sugar solutions is presented as percent of control and shown in Table 1 and Figure 10. Statistical results (F value) showed that the effect of sugars with different amino acids was significant at $P \leq 0.01$. No significant difference was observed among

Table 1. Color development of fried filter paper disks impregnated with buffered amino acid-sugar solutions¹, as presented by % of control.

Group ²	Amino acid ³	Agtron number ⁴ (% of control)			
		Buffer	Fructose	Glucose	Sucrose
I	Control ⁵	100.00	100.00	100.00	100.00
	Lysine	84.65	52.33	52.00	48.64
	Glycine	87.78	57.83	55.58	50.78
	Tyrosine	88.29	59.84	59.19	55.42
	Average⁶	86.91a	56.67b	55.59b	51.61e
II	Leucine	88.15	70.00	69.70	78.07
	Isoleucine	88.52	69.67	70.17	84.04
	Methionine	88.52	68.33	71.30	90.02
	Average	88.40a	69.33c	70.39c	84.04f
III	Arginine	88.99	75.35	74.07	96.10
	Aspartic acid	88.75	71.85	74.35	98.99
	Glutamic acid	88.74	79.19	74.57	100.45
	Average	88.83a	75.46d	74.33d	98.51g

Coefficient of variation = 0.93%

¹ Amino acid-sugar molar ratio of 1:1, final concentration of 0.001M, pH 6.5. The filter paper disks were fried in vegetable oil at 180°C for 2 min.

² Group I, II, and III produce high, intermediate, and low Maillard browning, respectively (Ashoor and Zent, 1984).

³ All amino acids were L-isomers, found in greatest amounts in potato tubers.

⁴ Average of 3 readings, presented as % of control.

⁵ Filter paper disks impregnated with only buffer solution or buffered sugar solutions.

⁶ Means with the same letter are not significantly different at $P \leq 0.01$ using lsd.

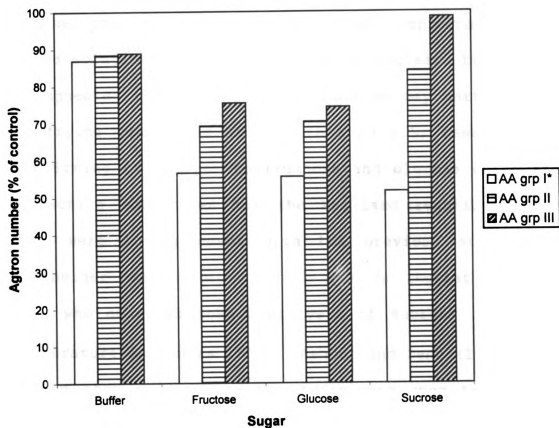


Figure 10. Color development of filter paper disks impregnated with buffered amino acid-sugar solutions (molar ratio 1:1), as presented by % of control.

* Amino acid groups I, II, and III produce high, intermediate, and low browning, respectively (Ashoor and Zent, 1984).

the amino acid-buffer systems ($P \leq 0.01$). Fructose/amino acid and glucose/amino acid systems were not significantly different. But both systems produced significantly darker colored disks than sucrose/amino acid systems. Although sucrose does not participate in the Maillard reaction, sucrose/amino acid systems resulted in darker colored disks than the control (filter paper disks impregnated with buffered solution). The reasons remain unclear, but it has been suggested that hydrolysis of sucrose may partly occur under frying conditions at 180°C and pH 6.5, resulting in the splitting of sucrose to fructose and glucose which are the reactive substrates for the Maillard reaction. The results were in agreement with the previous studies of Shallenberger and Moore (1957) and Leszkowiat et al. (1990), who observed that hydrolysis of sucrose can occur at temperature as low as 150°C . Ashoor and Zent (1984) also suggested that sucrose was not hydrolyzed upon heating in an autoclave at 121°C for 10 min. The color generation of sucrose systems may also due to the caramelization or other unknown reactions with components present in the oil at 180°C in the absence of water (Roe and Faulks, 1991).

Individual amino acids in combination with each sugar yielded varying degrees of Maillard browning. The amino acids were ranked according to color intensity of fried

paper disks as measured by the Agtron colorimeter. In a previous study, amino acids were classified into 3 groups according to the intensity of Maillard browning; high, intermediate, and low browning producing amino acids (Ashoor and Zent, 1984). Ranking of the browning intensity of amino acid/sugar systems was consistent with the previous work (Ashoor and Zent, 1984), except arginine yielded higher browning intensity than that of aspartic acid in the present study. Amino acids were classified based on their significant differences ($P \leq 0.01$) in browning intensity, as presented by percent of control, using least significant test (lsd). High browning producing amino acids include lysine, glycine, and tyrosine. Intermediate browning producing amino acids include leucine, isoleucine, and methionine. Low browning producing amino acids were arginine, aspartic acid, and glutamic acid.

Lysine produced the highest intensity as expected since it contains both α - and ϵ -amino groups on the structure, unlike other amino acids, which contain only an α -amino group. Although lysine is a basic amino acid, the relationship between Maillard browning intensity and the basicity of amino acid was not valid in the present study. The basic amino acid, L-arginine produced low browning

intensity as compared to the neutral amino acid such as glycine. The results from this model study suggest that tubers containing high browning producing amino acids including lysine, glycine, and tyrosine at consistent level of reducing sugars should produce darker chips.

Arginine, aspartic acid and glutamic acid yielded the lowest browning intensity. The reason behind the fact that these amino acids produced only a slight browning was unclear. However, Nafisi and Markakis (1983) also reported that the browning intensity of lysine-glucose and lysine-fructose systems (pH 8, 60°C, 58 h) was decreased by adding L-aspartic acid or L-glutamic acid. Willits et al. (1958) reported that arginine had no positive effect on browning and glutamic acid in the glucose solution did not cause a significant increase in browning at any pH value.

Filter paper disks impregnated with buffered sugar solutions (both reducing and nonreducing sugars) were darker than the control (buffer alone). This is due to caramelization of sugar that can occur upon frying, simultaneously as the Maillard reaction proceeds. Filter paper disks impregnated with buffered amino acid solutions, however, yielded only a slight color as compared to the control. The slight color developed in any buffer-amino acid systems was due to the Maillard reaction between each

amino acid and a small amount of free sugars present in filter paper disks. The low concentration of sugars in the disks limits its ability to react with the remaining excess amino acids.

1.2. Filter paper disks impregnated with potato juices

Average Agtron number of simulated potato chips was compared with that of actual potato chips (Table 2, Figure 11). The simulated chips were fried filter paper disks impregnated with potato juice from cultivars, Atlantic, Mainstay, Shepody, Snowden, and Superior, harvested in 1995. The order of browning intensity of simulated chips was in agreement with actual chips. Snowden and Atlantic processed into excellent actual potato chips (Agtron number > 60). Both simulated and actual chips from superior, Shepody, were less acceptable, respectively, and Mainstay produced unacceptable chips. Statistical results showed that actual potato chips from Snowden and Atlantic were significantly different ($P \leq 0.01$) from other cultivars.

2. Potato slices

According to the filter paper disk study, lysine, leucine, and aspartic acid were selected as representatives of high, intermediate, and low browning producing groups, respectively, for further study. Table 3 and Figure 12 show the effect of relative proportions of the

Table 2. Average agtron number of fried filter paper disks impregnated with potato juices of selected potato cultivars harvested in 1995, and potato chips (in order of decreasing fry color)¹.

Cultivar	Agtron number ^{2,3}	
	Filter paper	Potato chip
Snowden	57.6a	66.2a
Atlantic	52.1b	64.4a
Superior	49.2b	57.9b
Shepody	45.5b,c	50.5c
Mainstay	42.1c	42.5d

Coefficient of variation = 2.9%

¹ After frying in vegetable oil at 180°C for 2 min.

² Agtron number (average of 3 readings) > 60 = excellent;
56-60 = acceptable; 50-55 = marginally acceptable;
< 45 = unacceptable.

³ Means within a column with the same letter are not significantly different using lsd at $P \leq 0.05$.

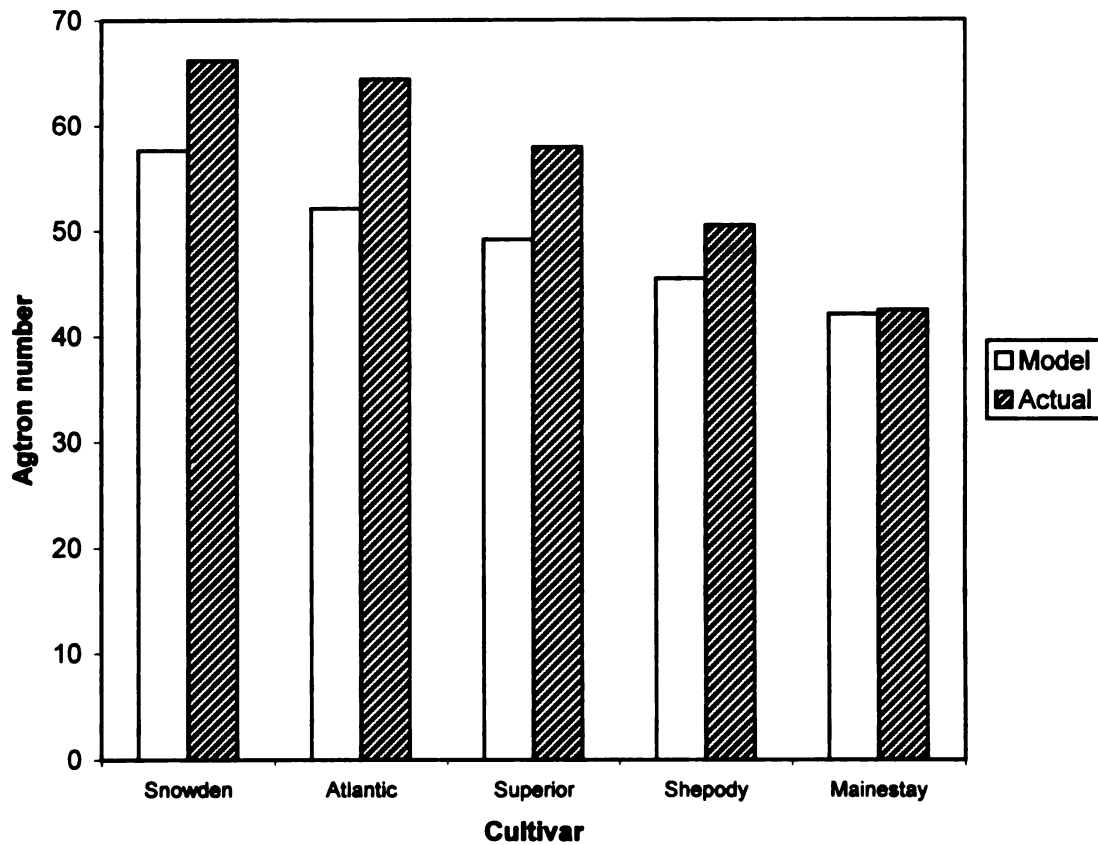


Figure 11. Color development of fried filter paper disks impregnated with potato juices and potato chips of selected potato cultivars, harvested in 1995.

Table 3. Average agtron number¹ of fried potato slices (Snowden) infiltrated with various molar ratios of buffered lysine, leucine, and aspartic acid-glucose systems.

Amino acid:Glucose	Agtron number ¹				
	Molar ratio of amino acid to glucose				
	0:0	1:1	2:1	5:1	10:1
Control ²	61				
Lysine:Glucose		36a ³	35a	31a,b	29b
Leucine:Glucose		45a	43a	37b	36b
Aspartic acid:Glucose		58a	54a	46b	43b

¹ Agtron number (average of 3 readings) > 60 = excellent; 56-60 = acceptable; 50-55 = marginally acceptable; < 45 = unacceptable

² Potato slices infiltrated with phosphate buffer solution, pH 6.5.

³ Means within a row with the same letter are not significantly different using lsd at $P \leq 0.05$.

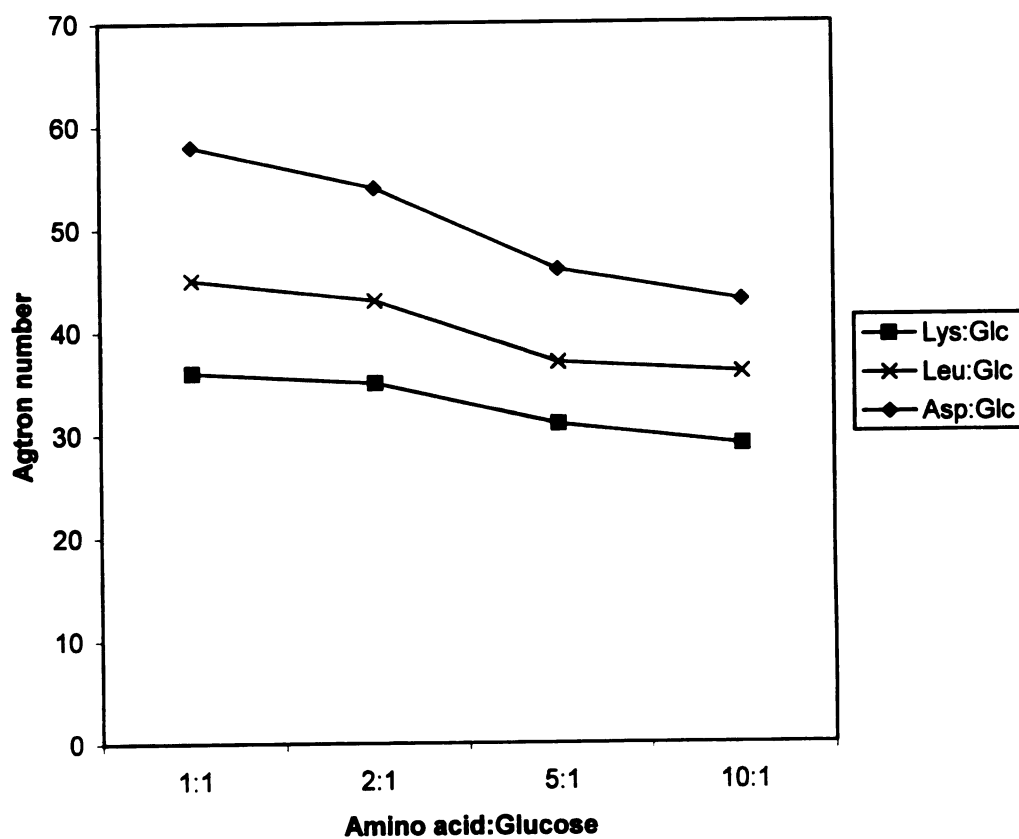


Figure 12. Average Agtron number of fried potato slices (Snowden) infiltrated with various molar ratios of buffered lysine, leucine, and aspartic acid-glucose systems.

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selected amino acids on Maillard browning. The free amino acid concentration in potatoes is in molar excess over that of total reducing sugars (Brierley et al., 1996). Kapoor et al. (1975) reported that the free amino acid concentration in potatoes is about 35-40 $\mu\text{mole/g}$ fresh tissue. Coffin et al. (1987) reported the total sugar concentration in potatoes about 10-15 $\mu\text{mole/g}$. The molar ratios applied in this study were based on the excessive concentrations of free amino acids compared with total reducing sugars. The results from this model study showed a pronounced effect of amino acid-sugar ratio on Maillard browning. Color development was relatively low at the amino acid-glucose ratios of 1:1 and 2:1, but is much greater at the ratios of 5:1 and 10:1. Statistical results showed that amino acid-glucose ratios of 1:1 and 2:1 were significantly different from those of 5:1 and 10:1.

Table 4 and Figure 13 show the effect of specific amino acids (lysine, leucine, and aspartic acid) on chip color made from slices infiltrated with these amino acids. Similar to the model filter paper disks, potato chips processed from slices infiltrated with lysine were darker than those with leucine and aspartic acid, respectively. There appeared to be no synergistic effect to increase browning among any of the amino acids tested. However,

Table 4. Average agtron number¹ of fried potato slices Snowden infiltrated with various combinations of buffered lysine, leucine, and aspartic acid-glucose systems².

Amino acid	Agtron number	
	w/o glucose	w/ glucose
Control ³	100	100
Lys	80a ⁴	53a
Leu	88b	72b
Asp	90b	102c
Lys + Leu	83a	56a
Lys + Asp	86b	80d
Leu + Asp	89b	89e

¹ Average of 3 readings, presented as % of control.

² Molar ratio of amino acid:sugar = 1:1,
amino acid:amino acid:sugar = 1:1:2.

³ Filter paper disks impregnated with only buffer solution or buffered sugar solutions.

⁴ Means within a column with the same letter are not significantly different using lsd at $P \leq 0.05$.

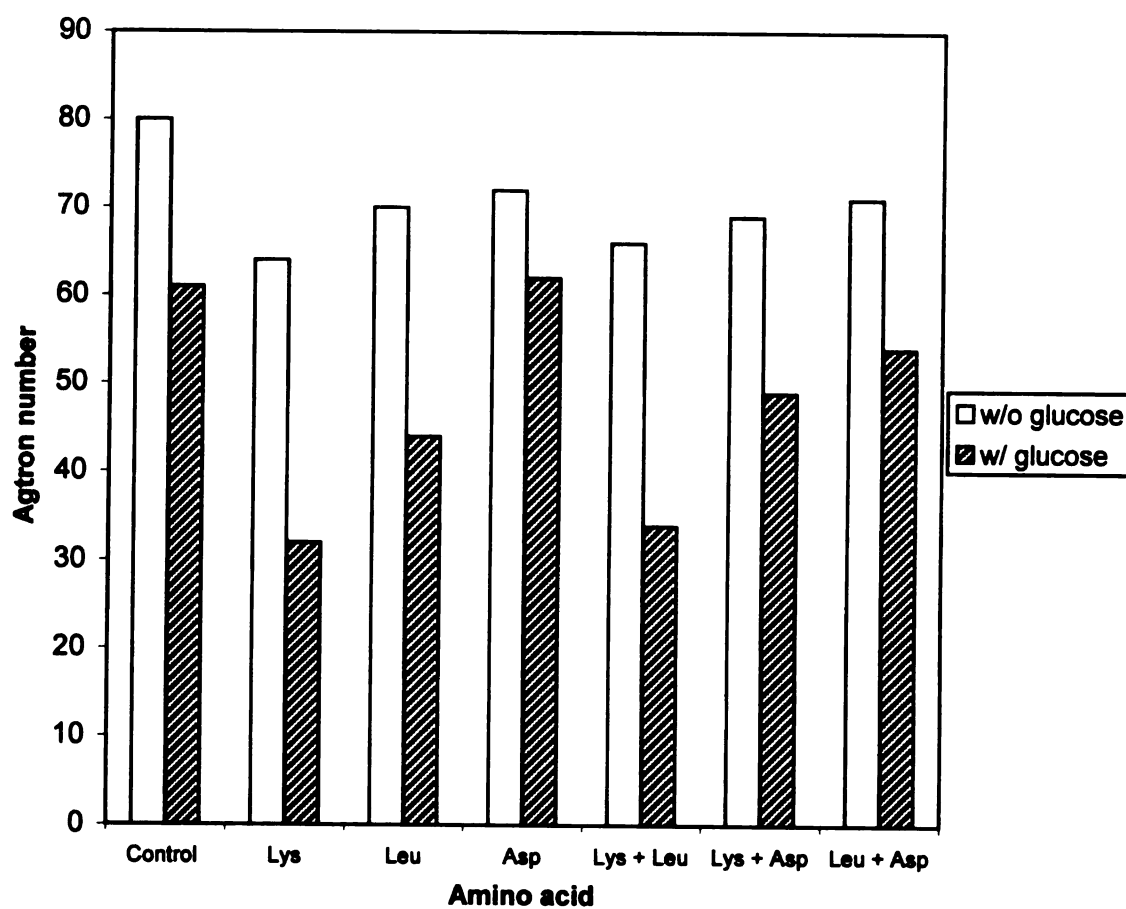


Figure 13. Average Agtron number of fried potato slices (Snowden) infiltrated with various combinations of buffered lysine, leucine, and aspartic acid-glucose systems.

when aspartic acid was combined with either lysine or leucine, there were significant reductions in browning. Previous work has shown this same effect of aspartic acid in decreasing browning intensity in lysine systems (Nafisi and Markakis, 1983).

CONCLUSION

The model studies simulating potato chip frying indicated that there are several factors affecting color development in potato chips. This study focussed on type, and relative concentration of amino acids and sugars. Different amino acid-sugar systems produced varying degrees of Maillard browning. Lysine, glycine, and tyrosine-sugar systems produced the highest browning intensity, while arginine, aspartic acid, and glutamic acid produced the least. Differences in degree of browning between fructose and glucose systems were not significant, but sucrose system produced only slight color.

The results from the model system studies showed the significant effect of type of amino acids on color development in simulated potato chips. Specific amino acids, lysine, glycine, and tyrosine, which produced the most intense browning, may be important factors governing the extent of reaction and intensity of chip color. Hence, the concentration of these amino acids present in tubers may be helpful in chip color prediction, as tubers

containing larger proportions of the high browning producing amino acids tend to produce poorer chips and vice versa.

However, in potatoes amino acids are present in excess of sugars, there may be no indication of specific amino acids reacting preferentially, as sugar is a limiting factor. In addition, potato tubers contain several components other than only amino acids and sugars present in the model systems. These unknown components may play an important role in chip color formation by enhancing or inhibiting the color reaction. Therefore, the second phase of this study was conducted with an attempt to determine the role of amino acids and sugars in color development in potato chips, based on the information obtained from the model system studies.

**ROLE OF AMINO ACIDS AND SUGARS IN COLOR OF POTATO CHIPS
MADE FROM SEVERAL GOOD AND POOR CHIPPING CULTIVARS**

ABSTRACT

Since Maillard reaction is primarily responsible for the color development in potato chips, this study was aimed at determining the relationships between chip color, glucose, free amino acids, and free amino groups in several good and poor chipping cultivars. Five potato cultivars, Atlantic, Mainstay, Shepody, Snowden, and Superior, harvested in 1995 and 1996, were analyzed monthly, for chip color, glucose, free amino acid, and free amino group contents. Free amino acid profiles of these cultivars at each storage period were compared. Snowden, and Atlantic, which are good chipping cultivars contained low amounts of glucose, free amino acids, and free amino groups. Mainstay, which is a poor chipping cultivar, contained the highest amount of glucose, and produced the darkest chips. In general, chips were darker as the glucose level increased, except in the cases of Shepody and Superior.

Shepody produced significantly darker chips than Superior, as it contained higher amounts of free amino acids, and free amino groups, although containing lower amounts of glucose. Shepody generally contained the highest amounts of high browning producing amino acids (lysine, glycine, and tyrosine), and produced the darkest chips. Snowden2 and 4 selections, ND2417-6, ND2471-8, NDA2031, and NDO1496, harvested in 1996 were also analyzed in terms of sugar, free amino acid, and free amino group contents. Snowden2 and all new selections except ND2471-8 contained low amounts of glucose, and produced acceptable chips throughout the storage period. Statistical analyses revealed that chip color correlated best when combining values for free amino acid, free amino group, and sucrose contents with glucose content ($R = 0.97$). Free amino group content appeared to be a better predictor for chip color than free amino acids and sucrose.

MATERIALS AND METHODS

Potatoes

In 1995: Five potato cultivars, Atlantic, Mainstay, Shepody, Snowden and Superior were grown on a sandy loam at the Montcalm Research Farm of Michigan State University in west central Michigan. All potato tuber samples were harvested at maturity in mid September 1995. All potato tubers were held at room temperature for 24 hours. The storage temperature for potato samples was at 12.8°C (55°F) with 90% RH for 3 weeks. Subsequently, storage temperature was reduced by 1°F every 2-3 days until the temperature reached 48°F. The samples were stored at 8.9°C (48°F) (90%RH) from September 1995 to February 1996.

In 1996: The same five potato cultivars as those harvested in 1995, Atlantic, Mainstay, Shepody, Snowden and Superior were grown at the Montcalm Research Farm and harvested at maturity in mid September 1996. Snowden2 and 4 new midwestern selections, ND2417-6, ND2471-8, NDA2031, and ND01496 were also grown in Montcalm, Michigan, and harvested at maturity. All new selections are thought to

be good chipping varieties, which tend to produce light colored chips. The new selections were also evaluated for chipping acceptability. All potato samples were held at room temperature for 24 hours. The samples were then stored at 12.8°C (55°F) (90%RH) for 3 weeks. The storage temperature was reduced to 8.9°C by 1°F every 2-3 day. Subsequently, the potato tubers were stored at 8.9°C with 90% RH for six months.

Potato chip frying

Every month potato chips were prepared from potato tubers stored at 48°F according to Gould and Plimpton (1985). Eight uniform sized tubers were randomly selected, peeled and washed. The potato tubers were sliced longitudinally with a manual slicer (The Eagle Tool and Machine Co., Inc., Springfield, OH) to approximately 0.125 to 0.175 cm thickness. Five slices from the center part were taken from each tuber. The total of 40 slices were washed with cold tap water and then fried in fresh vegetable oil at 180°C for 2 min with stirring after 1 min in a thermostatically controlled fryer.

Analytical methods

1. Sugar analysis

The preparation of samples for glucose and sucrose analysis was according to Sowokinos and Preston (1988) with slight modification. Eight average sized tubers were selected at random, peeled and washed. The center longitudinal pieces were taken from each tuber and cubed in half. Two hundred grams of tuber cubes were homogenized in an Acme juicerator (model #6001, Acme juicer Mfg, Co., Sierra Madre, CA). Three 100 mL volumes of cold distilled water were passed through the juicerator, by allowing 1-2 min between each wash. The potato extract was diluted to 430 mL with cold distilled water before refrigeration for approximately 1 hour. Ten mL of the extract was placed in the plastic vial and a 0.5 mL extract was automatically injected into the YSI-2700 analyzer (Yellow Springs Instrument Co., Yellow Springs, OH). The sugar content in the potato extract was analyzed in duplicate. Glucose and sucrose readings from YSI-2700 analyzer were in g/L. The calculation of glucose and sucrose content of potato extracts was as same as previously described in previous chapter.

2. Free amino acid analysis

A) Sample preparation

Eight uniform sized potato tubers were randomly sampled and peeled. Two hundred grams of potato tissue from the center part of each tuber was cubed and homogenized in an Acme juicerator. The potato juice was diluted to 150 mL with distilled water, and centrifuged at 3,500 rpm for 20 min. Solid phase extraction with a C18 Sep-Pak cartridge (Waters Corporation, Milford, MA) was used for sample clean-up. The solid phase extraction is an alternative technique for sample preparation other than ultrafiltration (UF). This technique may be used to clean up samples containing low molecular weight interference peaks. C18 Sep-Pak cartridges contain a non-polar bonded silica phase surface character (Cohen et al., 1989). The bonded phase of C18 Sep-Pak cartridge was solvated prior to use with 5 mL acetonitrile. The cartridge was then flushed with 10 mL HPLC-grade water. Two mL of potato juice were loaded into a Sep-Pak with a plastic syringe. The first components containing free amino acids and salts were eluted first with two 1 mL HPLC-grade water. The sample eluted from the cartridge was collected into a plastic vial for immediate further analysis. Flow rate for sample loading and elution was at 6 mL/min.

B) Free amino acid analysis

Chemicals- Phenylisothiocyanate (supplied in 1-mL vacuum-sealed ampules, triethylamine (sequanal-grade), a standard mixture of amino acids containing 2.5 μ mole/mL each in 0.1N HCl, a kit of individual amino acid standards, acetonitrile and methanol were the HPLC-grade products. All chemicals were from Sigma Chemical Company (St. Louis, MO).

Coupling with PITC- The Pico-Tag method (Millipore Corporation, Bedford, MA) was used for amino acid analysis. One hundred microliters of potato extract samples and 20 μ L of standard mixture of amino acids were placed in a 6 x 50 mm tubes and dried by rotary evaporation. The potato extract was dried soon after sample preparation to prevent enzymatic browning which may interfere the separation. To the dried sample 20 μ L of 90% ethanol was added and dried again to remove solvents and volatile components. To the residual amino acids 20 μ L of redry solution (ethanol:H₂O:triethylamine, 2:2:1) was added to neutralize any residual acid that may cling to glass tube. To the sample 20 μ L of a derivatizing solution(ethanol: H₂O: triethylamine: phenylisothiocyanate, 7:1:1:1) was added. The sample solution was vortexed, allowed to stand at room

temperature for 10 min, and vacuum evaporated to dryness. The coupling step allows amino acids to react with PITC to form Phenylthiocarbamyl amino acid (PTC-AA). To the residual amino acids a 200 μ l Pico-Tag sample diluent was added to reconstitute sample. The mixture was vortexed and centrifuged for 2 min. Ten μ L of the supernatant was automatically injected into the analyzer.

Reverse-Phase HPLC separation- The HPLC system (Waters Corporation, Milford, MA) consisted of the model 710B Waters WISP solvent delivery system, a 3.9 x 300 mm Pico-Tag column and a model 440 UV-Visible wavelength detector at 254 nm. Separation of the amino acids was performed by standard gradient elution. The mobile phase gradient was formed using a programmable pump unit. The mobile phase consisted of Pico-Tag Eluents A and B (Waters Corporation, 1989). Eluent A contained 19 g of sodium acetate trihydrate, 0.5 mL of triethylamine, and 200 μ L of EDTA in 1 liter of water. The solution was adjusted to pH 6.4 with acetic acid. Eluent B consisted of 600 mL of acetonitrile and 400 mL of water.

Calculation

The results reported by the integrator/data system are typically in picomoles. The number can be converted into other units according to the following equations:

$$\frac{\mu\text{Moles}}{\text{Liter}} = \frac{\text{Picomoles}}{V_i} \times \frac{V_r}{V_d} \times \text{Dilution factor} \times \frac{10^6 \mu\text{L/L}}{10^6 \text{pMoles}/\mu\text{Mole}}$$

$$\frac{\mu\text{Moles}}{\text{gram}} = \frac{\text{Picomoles}}{V_i} \times \frac{V_r}{V_d} \times \frac{V_e}{\text{Wt. (g)}} \times \frac{10^6 \mu\text{L/L}}{10^6 \text{pMoles}/\mu\text{Mole}}$$

Where:

Picomoles = amount of component reported in the sample

V_i = injection volume

V_r = volume of diluent used to reconstitute sample

V_d = volume derivatized

Wt. = weight in gram of the sample

3. Free amino group analysis

Ninhydrin assay- Ninhydrin reaction was used to determine the concentration of free amino groups in potato extract samples. The procedure of Friedman et al. (1984) was used with slight modification. Ninhydrin was prepared freshly by dissolving 2.0g ninhydrin and 0.3g hydrindantin in 75 mL dimethyl sulfoxide (DMSO). To the mixture was then added 25 mL of 4M lithium acetate buffer, pH 5.2. Two mL of

potato juice sample as prepared for free amino acid analysis was loaded into the C18 Sep-Pak cartridge (Waters Corporation, Milford, MA), followed by 5 mL of distilled water. The Sep-Pak was flushed with 5 mL acetonitrile, followed by 15 mL of distilled water prior to sample loading. First component was eluted with two 1 mL distilled water. One mL of the component eluted from the cartridge was mixed with 1 mL of ninhydrin solution in a medium-sized test tube. The tube was vortexed and then heated in a boiling water bath for 15 min. To the cool reaction solution was added 6 mL of 50% ethanol-water. The tubes were vortexed and any insoluble particles were removed by centrifugation. The absorbance of a cool solution at 570 nm was measured with an Ultraspec II LKB Biochrom spectrophotometer against a reagent blank in a 1 cm pathlength cuvette. The mixture was diluted with additional 50% ethanol to place the absorbance in the most sensitive range (0.2-0.9) of the spectrophotometer. The concentration of free amino groups was determined using the standard curve of leucine. A standard curve was constructed in similar manner previously described in Moore and Stein (1954). One mL-samples of leucine at six concentrations from 0.05 to 0.2 mM were prepared in 0.1M citrate buffer at pH 5.

4. Chip color measurement

Color of potato chips was measured using the Agtron process analyzer model M-35-D (Agtron Inc., Sparks, NV). The Agtron process analyzer is an abridge spectrophotometer designed to measure specific spectral characteristics commercially used on potato chip samples (Agtron Inc., 1990). Agtron readings correspond to chipping quality of potatoes as follows: > 60 = excellent, 56-60 = acceptable, 50-55= marginally acceptable, < 45 = unacceptable. Agtron readings also correspond to color codes on the Potato Chip/Snack Food Association color chart as follows: > 65 = 1, 55-64 = 2, 45-54 = 3, 35-44 = 4, and 25-34 = 5.

5. Statistical Analysis

Single and multiple regression analyses were performed using SPSS program, version 6.1. The statistical relationships between various factors were reported in terms of correlation coefficients and coefficients of determination. The analysis of variance (ANOVA) was performed using Statview computer program.

RESULTS AND DISCUSSION

Sugar content

Table 5 shows the glucose and sucrose contents and the chip color of 5 cultivars (Atlantic, Mainstay, Shepody, Snowden, and Superior) harvested in 1995 and 1996. Changes in glucose content of tubers during storage are shown in Figures 14 and 15. Glucose content generally increased during storage in Mainstay, Shepody, and Superior. Sowokinos and Preston (1988) suggested glucose content for chipping cultivars to be 0.35 mg/g fresh weight and sucrose content (SR value) to be 1.0 mg/g fresh weight, respectively. Snowden and Atlantic, which are good chipping cultivars, contained glucose less than 0.35 mg/g fresh weight and sucrose generally below 1.0 mg/g fresh weight throughout the storage period in both harvest years (1995 and 1996). Mainstay harvested in 1995 was significantly higher in glucose (0.9-1 mg/g fresh weight) when compared to the other cultivars. In 1996, Mainstay contained glucose greater than 1 mg/g fresh weight at 90 days of storage.

Table 5. Sugar content (mg/g fresh weight) and chip color of 5 potato cultivars, harvested in 1995 and 1996, at 0, 30, 60, and 90 days of storage.

Cultivar ¹	Storage time (days)	1995				1996			
		Sugar content (mg/g) ²		Agtron no. ³		Sugar content (mg/g) ²		Agtron no. ³	
		Glucose	Sucrose			Glucose	Sucrose		
Snowden	0	0.138	0.891	66.2		0.024	0.596	63.3	
	30	0.135	0.814	64.3		0.181	0.978	56.4	
	60	0.145	1.032	61.1		0.075	0.750	56.2	
	90	0.157	0.950	56.3		0.034	0.836	56.3	
Atlantic	0	0.132	0.823	64.4		0.148	0.989	60.0	
	30	0.124	0.491	63.0		0.151	0.877	58.8	
	60	0.151	0.584	60.7		0.073	0.735	56.5	
	90	0.153	0.842	55.8		0.071	0.808	55.4	
Superior	0	0.621	0.763	57.9		0.080	0.718	57.9	
	30	0.615	0.660	55.8		0.243	0.694	51.7	
	60	0.822	0.822	51.9		0.621	0.559	50.8	
	90	0.859	1.171	50.7		0.854	0.649	49.3	
Shepody	0	0.502	0.650	50.5		0.144	0.897	55.8	
	30	0.494	0.513	48.6		0.385	1.359	51.1	
	60	0.785	0.962	44.3		0.624	0.862	50.1	
	90	0.994	1.284	42.4		N/A	N/A	49.2	
Mainestay	0	0.896	0.644	42.5		0.248	0.677	59.7	
	30	0.984	0.170	42.0		0.654	1.273	52.3	
	60	1.078	0.543	39.6		0.568	0.690	47.0	
	90	N/A	N/A	N/A		1.034	1.148	41.6	

¹ In order of decreasing average chip color.

² Average of two determinations.

³ Agtron number (average of 3 readings) > 60 = excellent; 56-60 = acceptable; 50-55 = marginally acceptable; < 45 = unacceptable.
N/A (not available), as sprouting started in Mainestay, harvested in 1995 at 90 days of storage; experimental error occurred in sugar analysis of Shepody, harvested in 1996 at 90 days of storage.

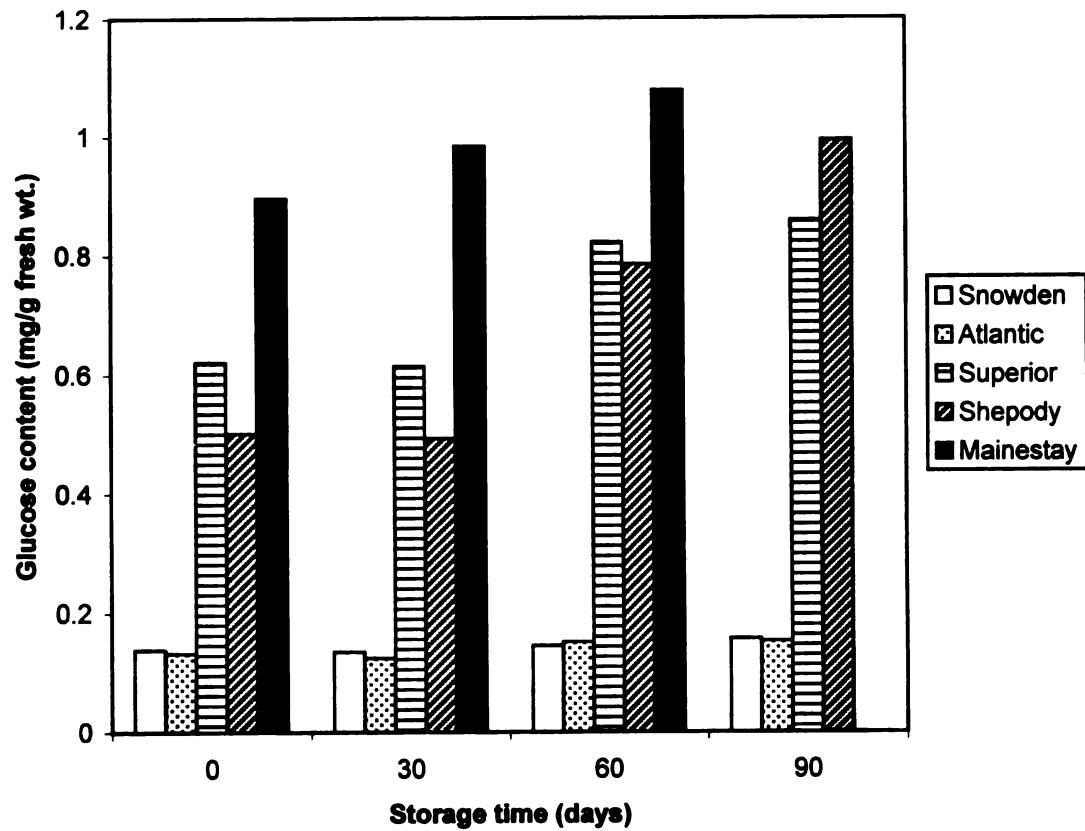


Figure 14. Glucose content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1995, at 0, 30, 60, and 90 days of storage.

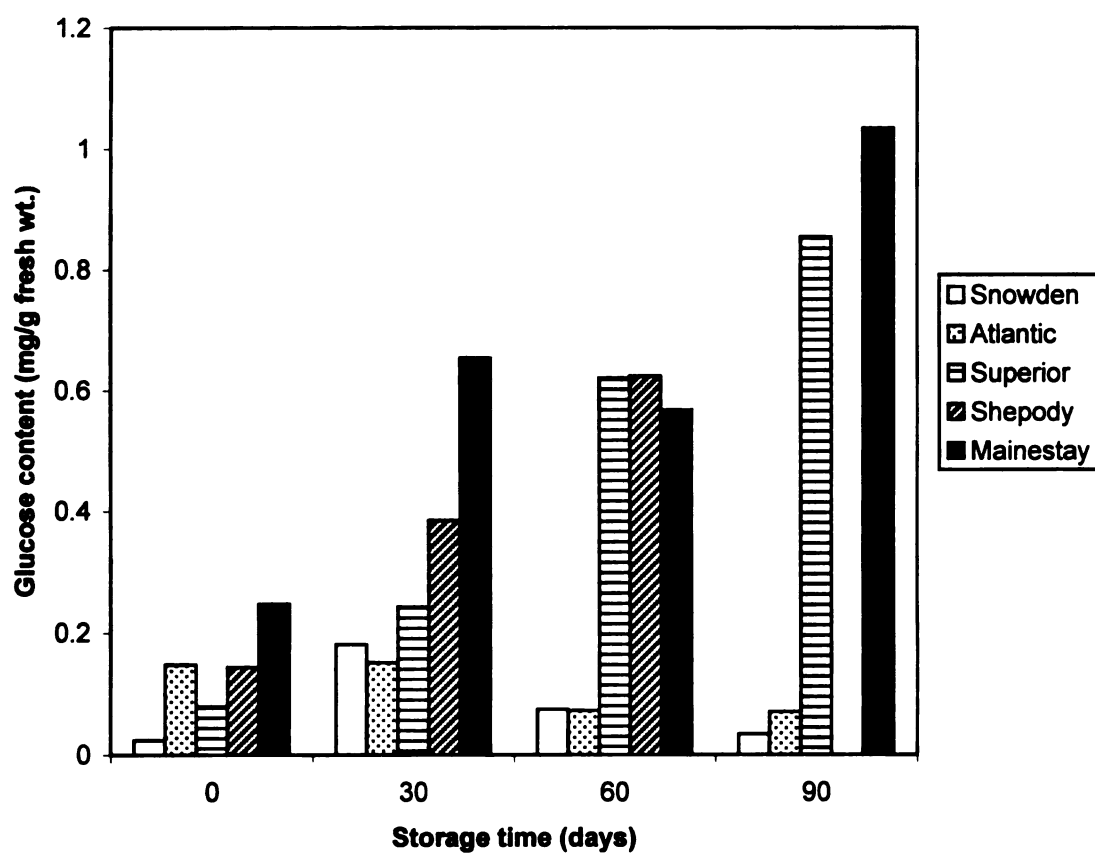


Figure 15. Glucose content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1996, at 0, 30, 60, and 90 days of storage.

Figures 16 and 17 show the Agtron chip color of cultivars, Atlantic, Mainstay, Shepody, Snowden, and Superior, harvested in 1995 and 1996, respectively. Chip color is thought to be determined by the total reducing sugar content since both glucose and fructose are involved in the Maillard reaction. However, because the ratio of glucose to fructose (1:1) are similar in most potato samples, the correlations between chip color and these sugars and total reducing sugar are similar. Thus only glucose content measured by YSI method used in this experiment would be an accurate indication of total reducing sugars in most cases. In both seasons, Snowden and Atlantic produced the lightest colored chips since they were low in glucose. Mainstay, which contained the highest amounts of glucose, produced the darkest colored chips as expected. In general, chips were darker as the level of glucose increased, and vice versa. However, in some cases chips made from tubers containing low amounts of glucose were unacceptable. Although Shepody generally contained lower amounts of glucose than Superior, it produced significantly darker chips. This situation may be due to variations in free amino acids in potatoes (Roe et al., 1990). The correlation coefficients (r) between glucose content and chip color was 0.90.

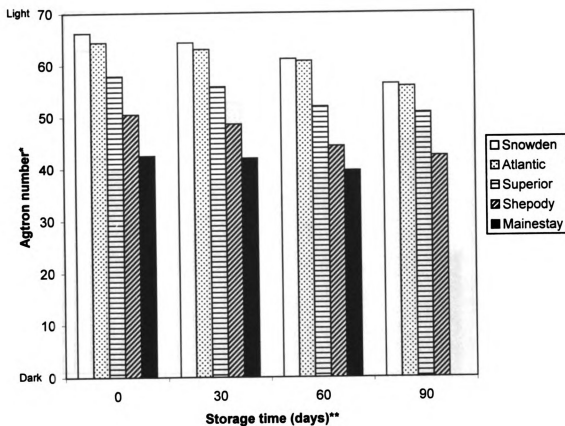


Figure 16. Agtron chip color of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1995, at 0, 30, 60, and 90 days of storage.

*Agtron number > 60 = excellent; 56-60 = acceptable; 50-55 = marginally acceptable; < 45 = unacceptable.

** Missing data due to experimental error.

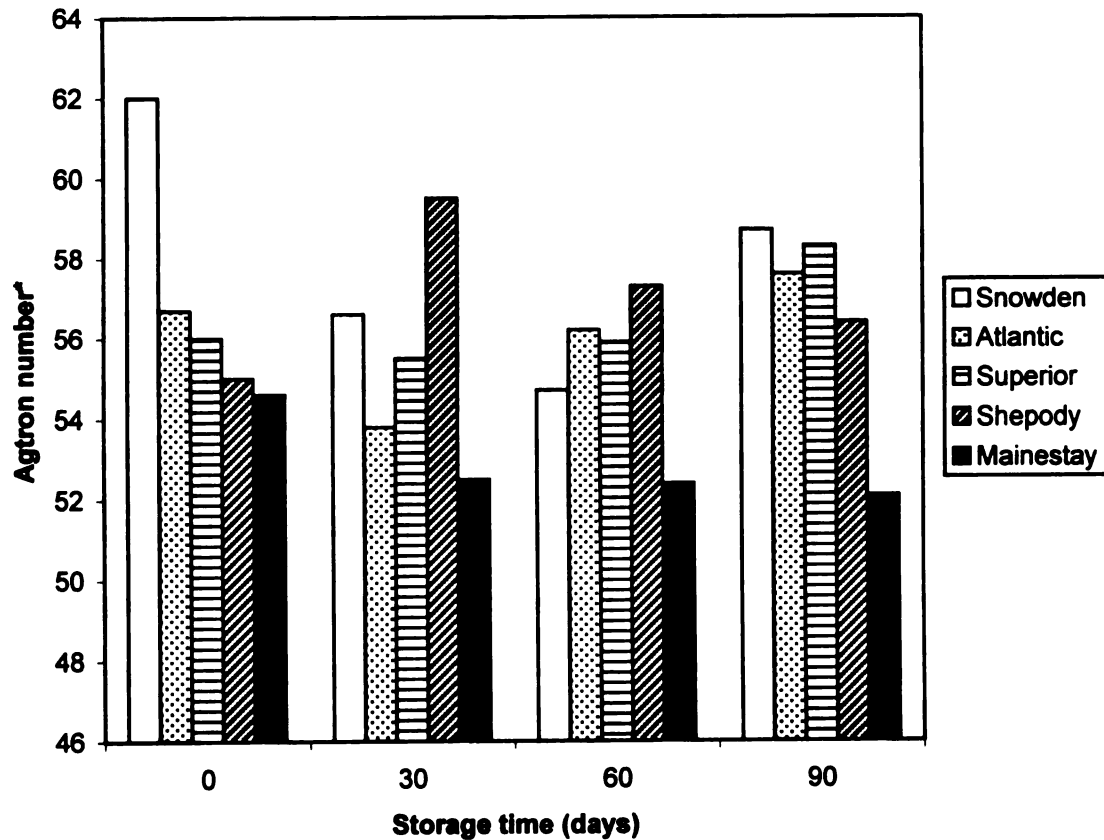


Figure 17. Agtron chip color of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1996, at 0, 30, 60, and 90 days of storage.

*Agtron number > 60 = excellent; 56-60 = acceptable; 50-55 = marginally acceptable; < 45 = unacceptable.

Changes in sucrose during storage in 1995 and 1996 of cultivars, Atlantic, Mainstay, Shepody, Snowden, and Superior are shown in Figures 18 and 19, respectively. In general, all cultivars achieved an SR value below 1.0 in most storage times. As expected, sucrose content was poorly correlated with chip color ($r = 0.133$), because sucrose does not participate in the Maillard reaction.

Differences in glucose content due to the effects of cultivar, and storage time were significant at $p \leq 0.01$ and $p \leq 0.05$, respectively (Table A1). But there was no significant effect of cultivar x storage time interaction. The effect of cultivar, storage time and the interactive effect of cultivar x storage time on sucrose content were not significant ($p > 0.05$).

Sugar (glucose and sucrose) contents of Snowden2 and 4 selections, ND2417-6, ND2471-8, NDA2031, and NDO1496 are shown in Table 6, Figures 20 and 21. Snowden2 and all selections contained glucose less than 0.35 mg/g fresh weight and achieved an SR value below 1.0, and produced acceptable chips throughout the storage period. Snowden2 is a good chipping cultivar, while these 4 selections are thought to produce good chips. Significant differences on glucose ($p \leq 0.05$) and sucrose ($p \leq 0.01$) were due to the

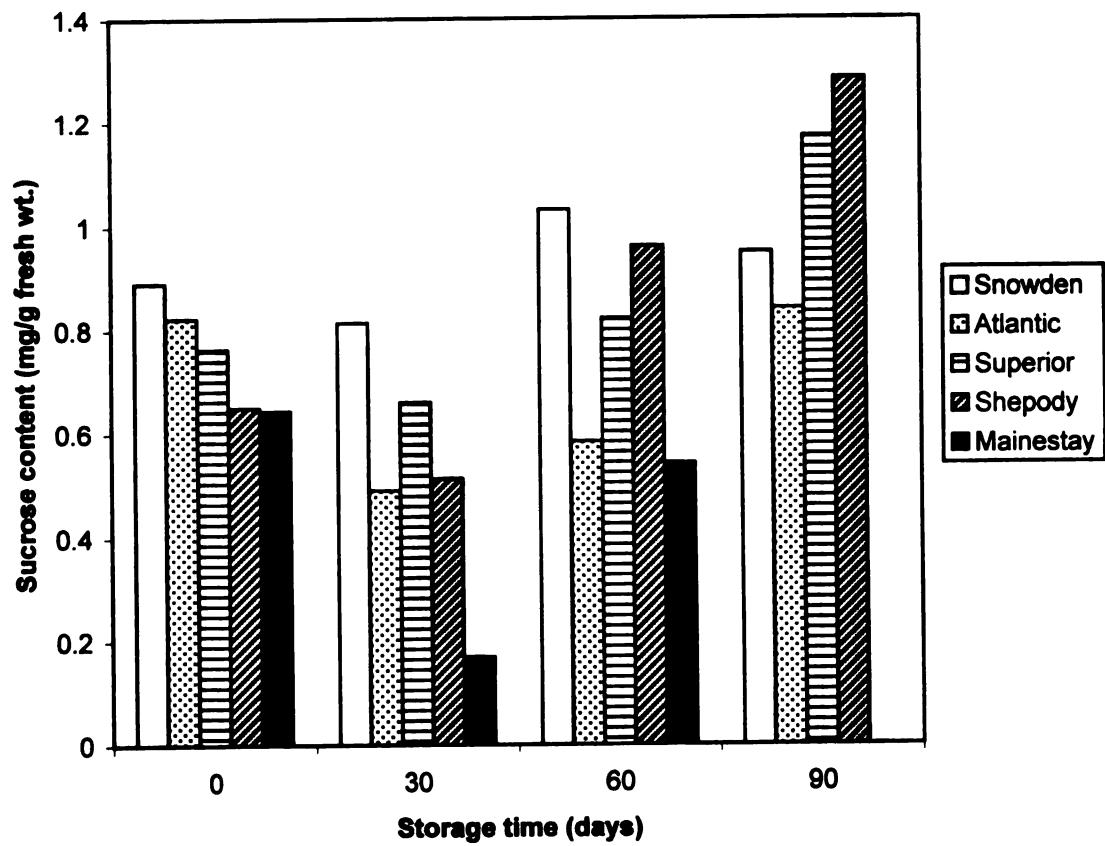


Figure 18. Sucrose content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1995, at 0, 30, 60, and 90 days of storage.

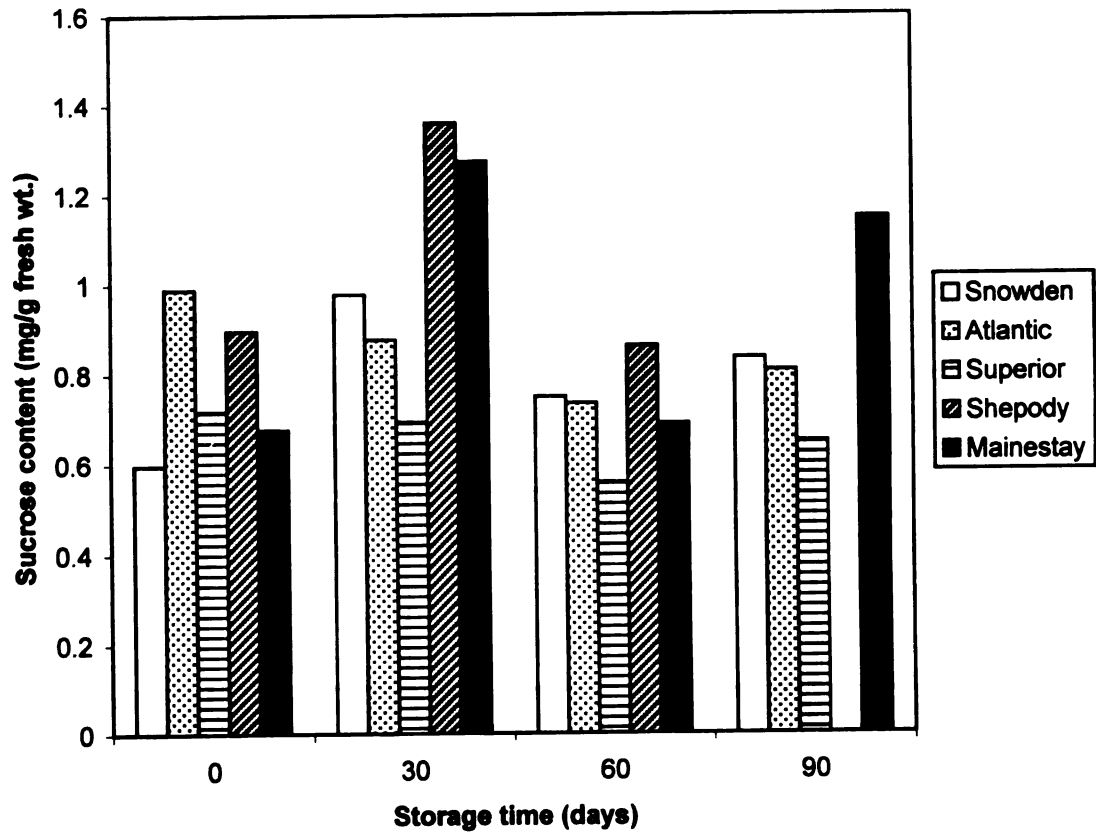


Figure 19. Sucrose content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1996, at 0, 30, 60, and 90 days of storage.

Table 6. Sugar content (mg/g fresh weight) and chip color of Snowden2 and, 4 selections, harvested in 1996, at 0, 30, 60, and 90 days of storage.

Cultivar	Storage time (days)	Sugar content (mg/g) ¹		Agtron no. ²
		Glucose	Sucrose	
Snowden2	0	0.017	0.649	62.0
	30	0.172	0.783	56.6
	60	0.088	0.677	54.7
	90	0.073	0.742	58.7
ND2417-6	0	0.075	0.617	55.0
	30	0.065	0.492	59.5
	60	0.123	0.413	57.3
	90	0.073	0.499	56.4
ND2471-8	0	0.028	0.510	54.6
	30	0.108	0.864	52.5
	60	0.108	0.808	52.4
	90	0.135	0.922	52.1
NDA2031	0	0.049	0.589	56.0
	30	0.052	0.456	55.5
	60	0.129	0.550	55.9
	90	0.080	0.522	58.3
NDO1496	0	0.019	0.604	56.7
	30	0.054	0.439	53.8
	60	0.062	0.460	56.2
	90	0.019	0.449	57.6

¹ Average of 2 determinations.

² Agtron number (average of 3 readings) > 60 = excellent;
56-60 = acceptable; 50-55 = marginally; < 45 = unacceptable.

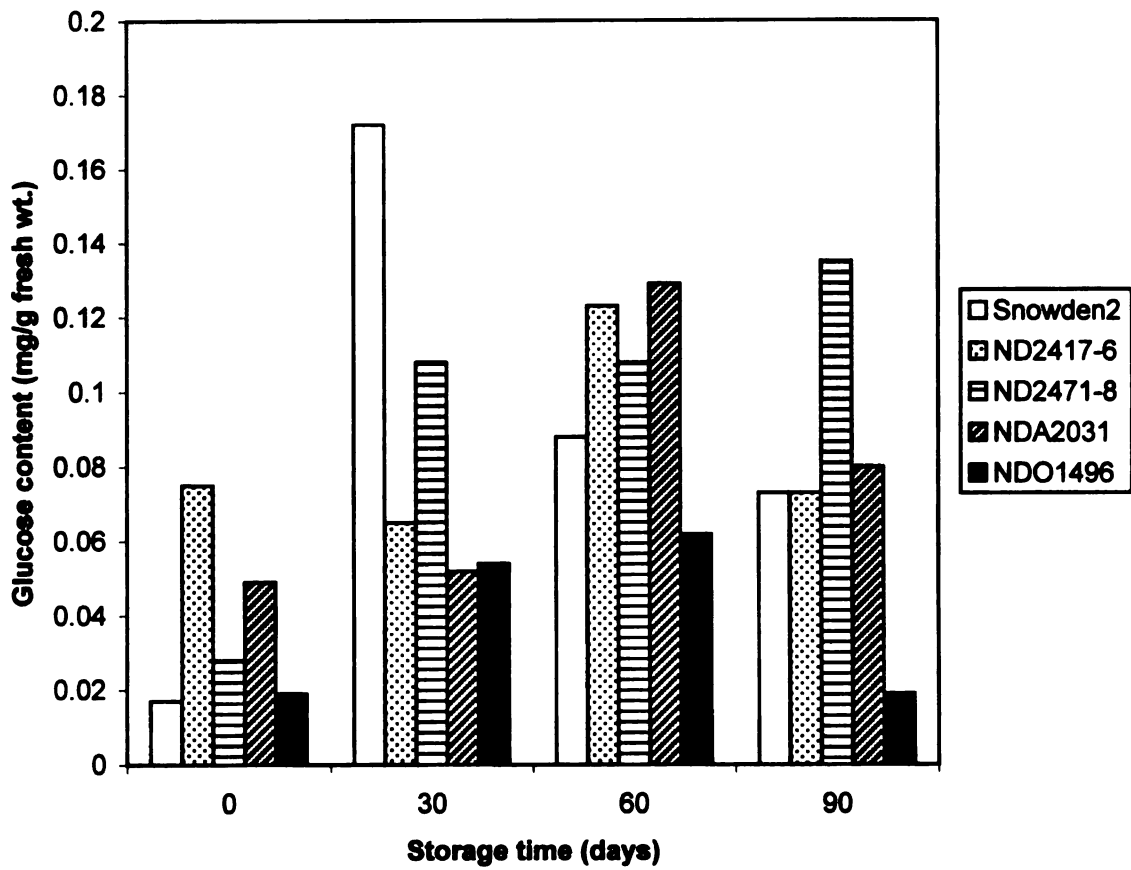


Figure 20. Glucose content of Snowden2, and selections, ND2417-6, ND2471-8, NDA2031, and NDO1496, harvested in 1996, at 0, 30, 60, and 90 days of storage.

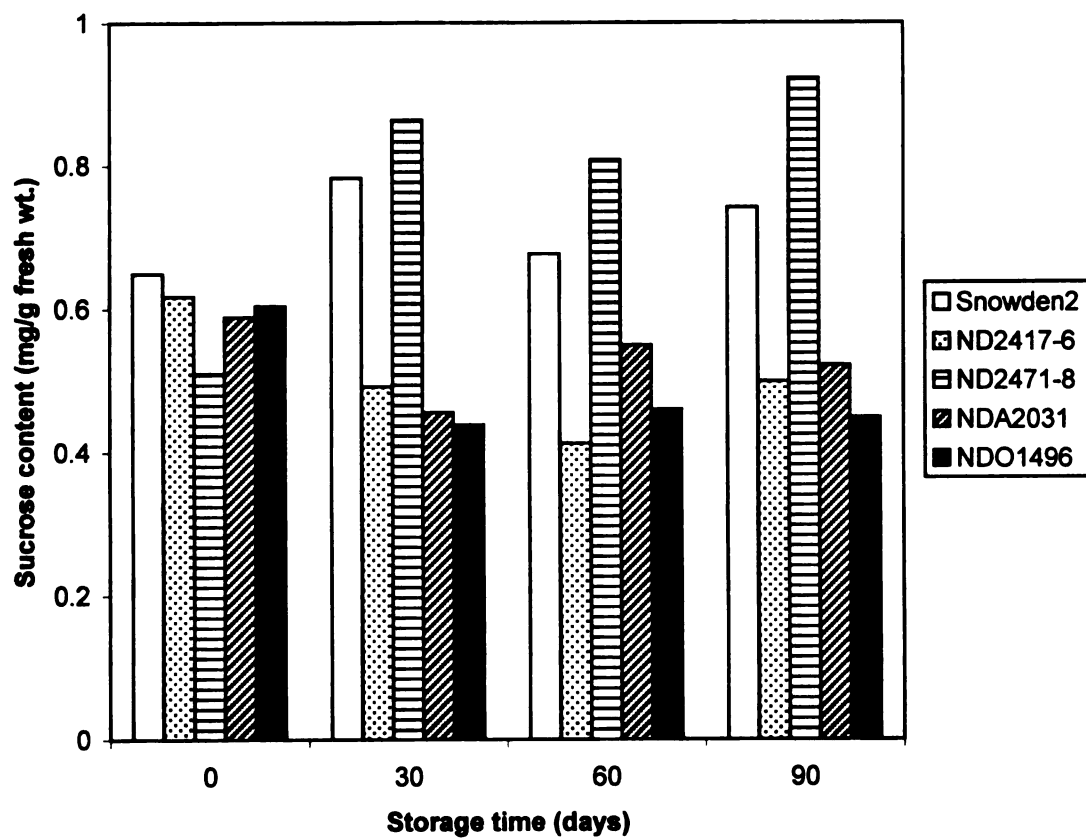


Figure 21. Sucrose content of Snowden2, and selections, ND2417-6, ND2471-8, NDA2031, and NDO1496, harvested in 1996, at 0, 30, 60, and 90 days of storage.

effects of cultivar, storage time, and their interaction.

Total free amino acid content

Tables 7 and 8 show the free amino acid composition of potato tubers, cultivars, Atlantic, Mainstay, Shepody, Snowden, and Superior during storage in 1995 and 1996, respectively. In addition to individual amino compound contents, total free amino acid content in tubers is also reported.

In all cultivars and both harvest seasons, total free amino acid content generally increased over the storage period, which was consistent with the finding of Brierley et al. (1996). The accumulating of free amino acids is due to the breakdown of protein by proteinase enzyme, for providing an energy supply for tubers. Brierley (1996) also reported an increase of proteinase activity, which was consistent with the accumulation of free amino acids and a decrease of chipping quality in Pentland Dell at 10°C. Figures 22 and 23 show the total free amino acid composition of potatoes in 1995 and 1996, respectively. In general, Snowden contained the lowest amounts of total free amino acids, followed by Atlantic. As expected, Snowden and Atlantic, which contained the lowest amounts of glucose (<0.35 mg/g fresh weight) and total free amino acids in

Table 7. Free amino acid content (nmole/g fresh wt.) of 5 potato cultivars, harvested in 1995 at 0, 30, 60, and 90 days of storage.

Group ¹	Amino Acid	Free amino acid content (nmole/g fresh wt.) ²											
		Snowden				Atlantic				Superior			
		0	30	60	90	0	30	60	90	0	30	60	90
I	Lys	0.6	246.1	274.7	N/A	1.0	135.5	288.7	N/A	90.4	223.5	246.8	140.9
	Gly	2.3	180.4	82.1	N/A	2.7	151.3	132.0	N/A	77.8	148.8	101.8	598.2
	Tyr	0.7	111.4	86.7	N/A	38.2	123.3	196.4	N/A	115.4	177.5	112.2	323.8
	Sum	3.6	537.9	443.4	N/A	41.8	410.2	617.1	N/A	283.6	549.9	460.8	1062.8
II	Pro	36.3	43.4	237.6	N/A	2.4	14.6	199.5	N/A	10.1	335.2	69.5	247.6
	Leu	0.6	98.2	38.6	N/A	4.5	84.9	68.3	N/A	102.4	124.5	98.5	409.8
	Ile	0.3	196.8	77.3	N/A	7.9	179.5	113.8	N/A	143.3	215.1	198.3	278.6
	Ala	4.0	26.5	176.3	N/A	3.8	196.7	641.4	N/A	95.0	406.7	128.8	502.2
	Phe	0.1	104.2	1.0	N/A	161.2	0.8	71.2	N/A	1.3	88.1	101.3	246.7
	Met	0.6	160.6	72.8	N/A	3.1	276.4	70.3	N/A	105.5	118.6	164.2	17.2
	Val	3.7	455.8	221.6	N/A	3.3	442.4	300.2	N/A	370.5	416.2	462.3	343.7
	Ser	3.0	81.3	237.7	N/A	2.8	303.5	363.6	N/A	205.7	370.6	235.7	553.5
	Sum	48.6	1166.8	1062.9	N/A	189.0	1498.8	1828.3	N/A	1033.8	2074.9	1458.7	2599.2
III	His	2.3	52.0	143.8	N/A	5.2	178.8	124.9	N/A	63.9	136.8	227.8	48.4
	Thr	12.8	139.7	141.3	N/A	1.9	163.0	168.6	N/A	122.4	175.9	207.7	570.6
	Asp	42.5	1.6	382.6	N/A	5.3	340.9	474.8	N/A	286.1	265.4	501.1	301.5
	Arg	114.0	24.7	465.4	N/A	18.8	350.4	386.8	N/A	265.0	268.2	674.8	54.1
	Glu	6.4	1.6	278.6	N/A	1.3	273.8	161.4	N/A	178.3	87.3	225.9	332.7
	Sum	177.9	219.6	1411.7	N/A	32.5	1306.9	1316.6	N/A	915.7	933.6	1837.3	1307.4
Mainstay	Total	230.1	1924.4	2918.0	N/A	263.3	3215.9	3761.9	N/A	2233.1	3558.4	3756.8	4969.5
Shepody													
Mainstay													

¹ Group I, II, III produce high, intermediate, and low browning producing groups, respectively (Ashoor and Zent, 1984).

² Average of 2 determinations.

Table 8. Free amino acid content (nmole/mg fresh wt.) of 5 potato cultivars, harvested in 1996 at 0, 30, 60, and 90 days of storage.

Group ¹	Amino Acid	Free amino acid content (nmole/g fresh wt.) ²																									
		Snowden						Atlantic						Superior						Shepody						Mainstay	
		0	30	60	90	0	30	60	90	0	30	60	90	0	30	60	90	0	30	60	90						
I	Lys	3.0	16.8	27.8	7.4	N/A	20.1	24.6	7.0	15.1	12.2	N/A	6.5	0.4	343.5	692.0	690.7	1.2	30.0	31.1	N/A						
	Gly	83.0	52.8	55.9	209.7	24.3	44.4	61.8	79.6	48.5	53.8	N/A	171.0	183.6	560.4	236.2	240.5	19.7	40.0	36.2	N/A						
	Tyr	2.6	85.0	88.8	55.5	1.3	35.5	46.0	33.5	47.0	57.3	N/A	40.4	37.3	161.7	128.8	132.1	1.2	92.7	96.4	N/A						
	Sum	88.6	154.6	172.4	272.5	25.6	100.0	132.4	120.1	110.7	123.2	N/A	217.9	221.3	1065.6	1057.0	1063.3	22.2	162.7	163.8	N/A						
	II	Pro	13.7	63.5	69.8	9.6	6.5	189.1	213.9	7.7	203.1	293.3	N/A	11.9	16.5	510.4	865.7	896.7	5.5	64.0	65.8	N/A					
Leu		5.5	52.9	64.7	8.9	N/A	45.7	55.2	7.4	60.3	71.2	N/A	11.0	9.5	475.9	146.8	151.7	2.6	66.0	65.5	N/A						
Ile		4.4	126.8	159.7	8.2	5.7	118.0	142.5	8.9	151.8	177.7	N/A	7.8	7.0	76.7	282.7	287.3	2.6	166.6	165.9	N/A						
Ala		14.9	37.5	46.7	17.5	11.1	74.1	90.4	31.4	83.6	98.2	N/A	24.2	1840.4	189.7	331.4	342.2	6.4	52.8	51.5	N/A						
Phe		2.9	65.0	86.4	29.9	117.6	35.4	51.2	29.0	64.5	65.0	N/A	31.3	54.3	77.9	150.1	124.1	1.3	56.3	60.1	N/A						
Met		1.8	98.0	117.2	13.1	0.3	136.9	159.0	10.6	161.5	196.8	N/A	13.2	20.7	10.0	195.1	220.8	0.2	171.2	165.6	N/A						
Val		0.5	242.6	301.7	173.2	1.0	223.8	272.4	7.7	282.8	357.2	N/A	8.2	11.3	406.7	693.2	711.7	2.4	346.7	348.0	N/A						
Ser		10.1	32.5	44.4	2124.5	6.0	53.5	58.5	2035.1	36.2	38.0	N/A	2045.2	1971.0	340.5	364.1	375.7	4.2	37.9	36.8	N/A						
Sum		53.8	718.7	890.5	2384.9	148.2	876.5	1043.1	2137.7	1043.9	1297.4	N/A	2152.8	3930.7	2087.8	3029.1	3110.2	25.3	961.5	959.2	N/A						
III		His	4.2	50.1	63.2	73.8	3.1	60.9	70.5	80.3	30.5	37.1	N/A	110.8	68.0	149.4	169.9	172.2	1.8	65.0	66.9	N/A					
	Thr	5.6	51.2	48.6	258.6	5.1	26.1	29.0	188.2	18.6	25.5	N/A	305.9	370.9	258.0	293.8	288.3	2.5	32.6	34.1	N/A						
	Asp	8.8	86.1	138.9	35.0	7.4	100.4	123.1	30.7	65.6	60.0	N/A	36.2	32.4	519.5	357.0	359.1	6.2	52.5	55.0	N/A						
	Arg	6.4	98.1	160.7	31.9	4.4	164.4	194.5	5.6	61.7	54.5	N/A	44.0	37.8	220.8	708.3	741.8	2.9	120.7	119.1	N/A						
	Glu	11.5	131.2	195.9	27.7	8.8	187.9	222.4	22.4	98.0	102.5	N/A	20.1	21.5	575.7	458.4	457.7	6.4	93.3	94.8	N/A						
	Sum	36.6	416.7	607.3	427.1	28.8	539.7	639.5	327.3	274.4	279.5	N/A	517.0	530.5	1723.4	1987.3	2019.2	19.8	364.1	370.0	N/A						
Total		178.9	1290.0	1670.3	3084.5	202.5	1516.2	1815.0	2585.1	1429.0	1700.1	N/A	2887.7	4682.5	4876.9	6073.4	6192.7	67.3	1488.3	1492.9	N/A						

¹ Group I, II, and III produce high, intermediate, and low browning, respectively (Ashoor and Zent, 1984).

² Average of 2 determinations.

NA (not available) due to experimental error.

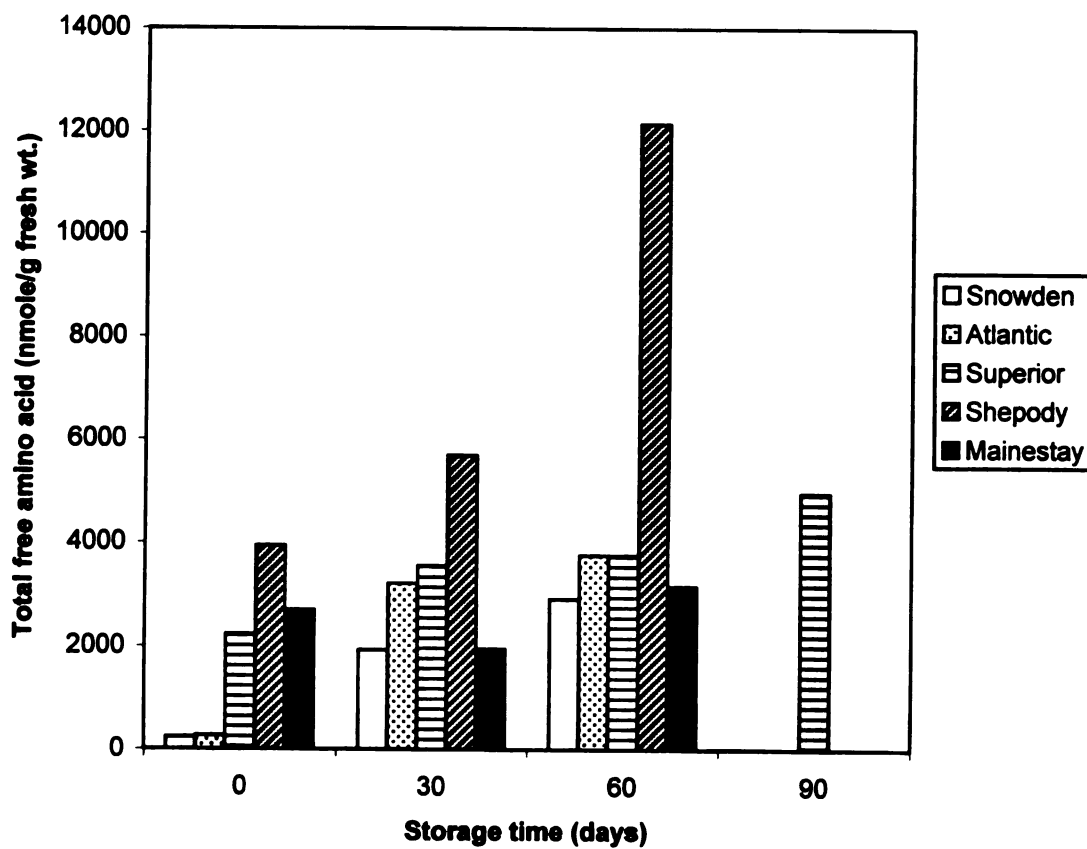


Figure 22. Total free amino acid content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1995, at 0, 30, 60, and 90 days of storage.

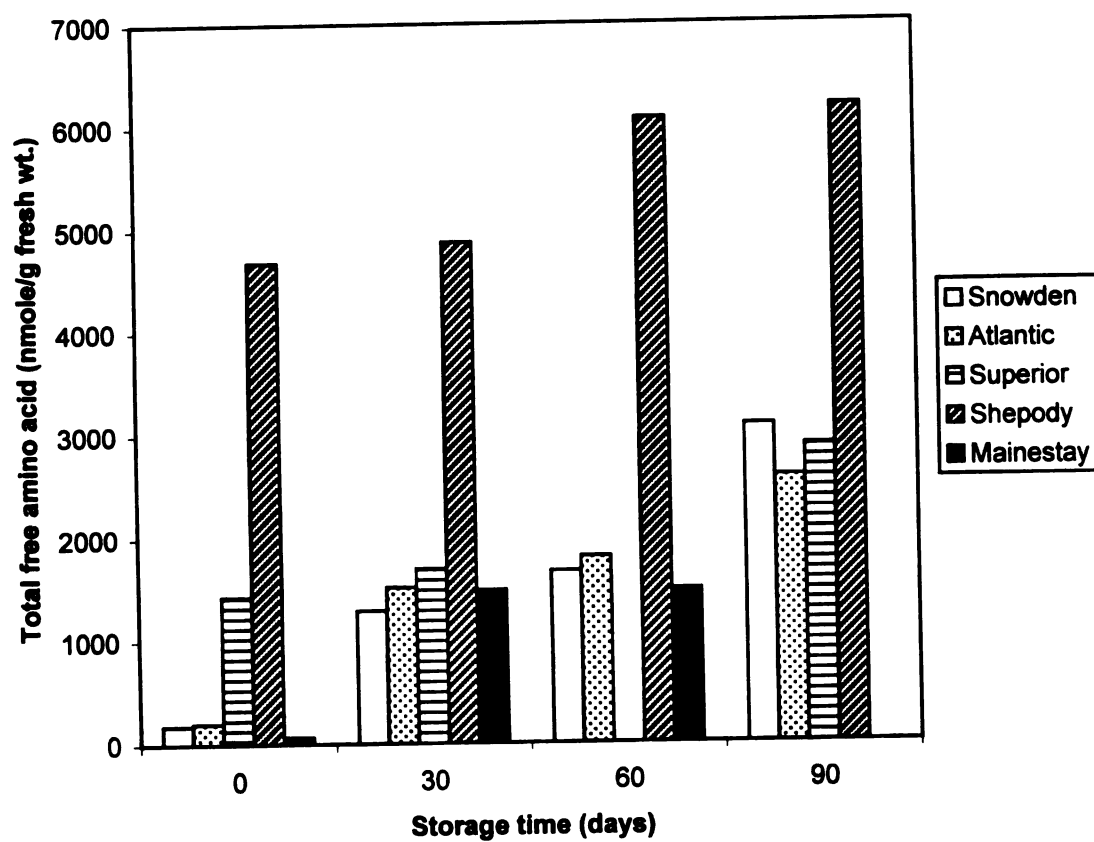


Figure 23. Total free amino acid content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1996, at 0, 30, 60, and 90 days of storage.

both harvest seasons, produced the lightest colored chips. Mainstay contained the highest amounts of glucose, although contained low amounts of total free amino acids, produced the darkest chips. These results suggest that reducing sugar is a limiting factor in color formation in potato chips since in potatoes amino acid are present in excess of sugars.

In 1995, total free amino acid content seems to be of importance in Shepody and Superior which contained glucose in the intermediate range (> 0.35 but < 0.9 mg/g fresh weight). In term of glucose content, Shepody contained significantly less amounts of glucose than Superior. But chips made from Shepody were unacceptable (Agtron no. < 50) while those from Superior were acceptable (Agtron no. > 50). The results suggest that free amino acid content present in potato tubers may be a critical factor affecting the general relationship between chip color and glucose content. Over the storage period, Shepody contained the highest amounts of total free amino acids. Unacceptable color of chips made from Shepody was due to the interaction between reducing sugars and high free amino acid content in the tubers.

Correlation coefficients (r) between chip color and total free amino acid content alone were as low as 0.47.

When combining total free amino acids with glucose, multiple correlation coefficient increased from 0.90 to 0.93. This statistical analysis indicated that total free amino acid content might be helpful in chip color prediction.

Analysis of variance (Table A1) showed significant differences ($p \leq 0.01$) in total free amino acid content for cultivar and storage time. No significant effect ($p \geq 0.05$) was observed for the interaction of cultivar x storage time.

Free amino acid compositions of Snowden2 and the 4 selections during storage are shown in Table 9 and Figure 24. The results showed an increase in free amino acids after 30 days of storage for Snowden2 and all the selections. The statistical results indicated that chip color was poorly correlated with total free amino acid content ($r = 0.075$).

High browning amino acids (Lysine, glycine, and tyrosine)

According to the model systems utilizing filter paper disks previously described, type and concentration of amino acids are important factors in chip color formation. Lysine, glycine, and tyrosine yielded the highest browning as compared to other amino acids. Therefore, tubers

Table 9. Free amino acid content (nmole/g fresh wt.) of Snowden2 and 4 selections, harvested in 1996 at 0, 30, 60, and 90 days of storage.

Group ¹	Amino Acid	Free amino acid content (nmole/g fresh wt.) ²											
		Snowden2				ND01496				NDA2031			
		0	30	60	90	0	30	60	90	0	30	60	90
I	Lys	28.2	157.9	365.2	344.4	75.1	131.8	212.7	198.9	N/A	45.2	186.7	187.2
	Gly	86.0	60.8	1380.5	1380.6	154.6	108.0	1366.3	1315.7	152.9	48.6	1262.8	1331.5
	Tyr	180.5	80.3	188.7	193.2	83.9	55.1	82.9	74.6	49.3	15.8	60.2	62.1
	Sum	294.7	299.0	1934.5	1918.2	313.5	295.0	1661.9	1589.2	202.2	109.6	1509.7	1580.9
										652.6	333.8	1876.9	1886.3
II	Pro	87.4	37.7	302.8	306.1	90.9	67.1	172.9	158.8	51.4	29.2	151.2	149.9
	Leu	83.8	34.8	77.8	78.5	66.7	43.2	53.7	48.6	58.6	28.8	47.8	48.1
	Ile	161.2	69.1	152.9	166.9	147.7	93.8	115.8	106.9	101.5	43.6	86.0	89.5
	Ala	45.1	21.1	782.3	799.3	48.4	30.1	507.9	586.5	41.1	14.7	955.9	989.3
	Phe	1.9	0.7	94.7	101.1	54.4	44.3	51.9	48.1	25.9	10.2	20.9	21.7
	Met	162.4	70.4	79.8	140.5	148.9	99.4	64.5	55.6	162.1	75.4	146.3	180.3
	Val	382.1	162.4	424.0	438.5	365.9	250.1	211.4	224.9	276.1	124.5	230.1	237.4
	Ser	227.4	103.6	1393.2	1390.0	123.7	86.4	1572.6	1539.7	186.1	74.8	1334.6	1308.9
	Sum	1151.2	499.8	3307.6	3420.9	1046.5	714.4	2783.8	2769.1	902.9	401.2	2972.8	3025.1
										2453.0	1127.0	4150.1	4194.1
III	His	169.4	77.5	268.2	279.0	114.3	76.4	247.3	227.2	85.7	37.9	188.1	192.2
	Thr	320.8	143.8	421.1	450.3	211.9	143.6	255.9	N/A	239.8	111.8	N/A	N/A
	Asp	1044.9	464.5	2062.0	1937.2	549.6	385.8	1886.9	1753.7	526.5	245.7	1655.5	1719.9
	Arg	1317.8	588.2	1256.1	1242.3	1031.7	710.9	1237.4	1177.4	710.9	323.8	778.2	802.3
	Glu	1463.5	646.7	1619.0	1642.4	784.1	521.1	1470.3	1415.6	268.5	71.5	953.2	1012.2
	Sum	4316.4	1920.7	5626.4	5551.3	2691.6	1837.9	5097.8	4573.8	1831.4	790.8	3575.1	3726.7
										2624.1	1528.8	4568.9	4639.7
	Total	5762.3	2719.6	10868.4	10890.3	4051.6	2847.2	9543.5	8932.1	2936.5	1301.6	8057.6	8332.6
										5729.8	2989.6	10595.8	10720.1
										6710.3	3750.0	10765.0	11071.9

¹ Group I, II, and III produce high, intermediate, and low browning, respectively (Ashoor and Zent, 1984).

² Average of 2 determinations.

NA (not available) due to experimental error.

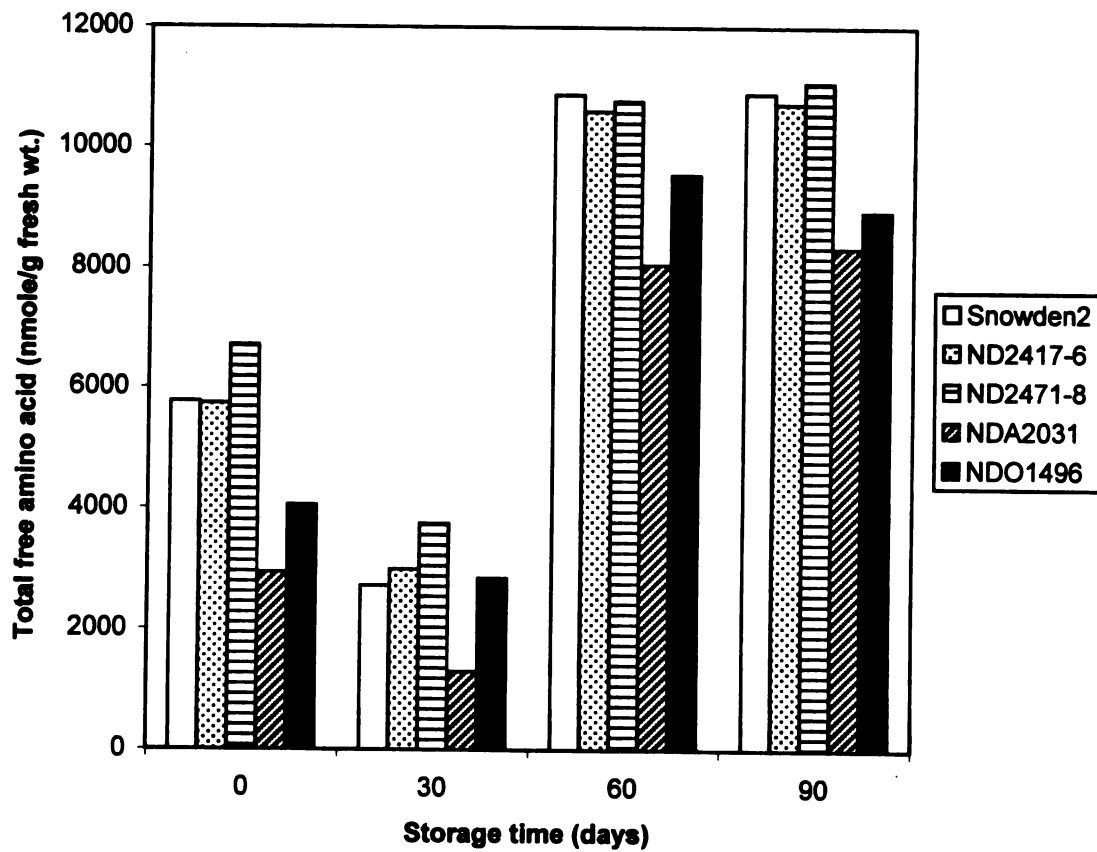


Figure 24. Total free amino acid content of Snowden2, and selections, ND2417-6, ND2471-8, NDA2031, and NDO1496, harvested in 1996, at 0, 30, 60, and 90 days of storage.

containing higher amounts of these amino acids are thought to be poorer chipping cultivars. Figures 25-26, Figures 27-28, and Figures 29-30 show lysine, glycine, and tyrosine content of cultivars, Atlantic, Mainstay, Shepody, Snowden, and Superior, harvested in 1995 and 1996, respectively. The total content of high browning producing amino acids (lys, gly, and tyr) in tubers, harvested in 1995 and 1996, are also reported (Figures 31 and 32, respectively). In both years, Shepody generally contained the highest amounts of lysine, glycine and tyrosine and produced unacceptable chips across the storage period except at fresh harvest (0 day). These results support the model system studies, which showed that lysine, glycine, and tyrosine produced high browning intensity. Other cultivars contained low amounts of lysine, glycine, and tyrosine and produced acceptable chips except Mainstay. Although containing low amounts of high browning amino acids, Mainstay produced the darkest chips since it contained the highest amounts of glucose. The results suggest that high browning producing amino acid content is significant in chip color in most cases, but not significant in tubers containing very high or low amounts of glucose such as Mainstay.

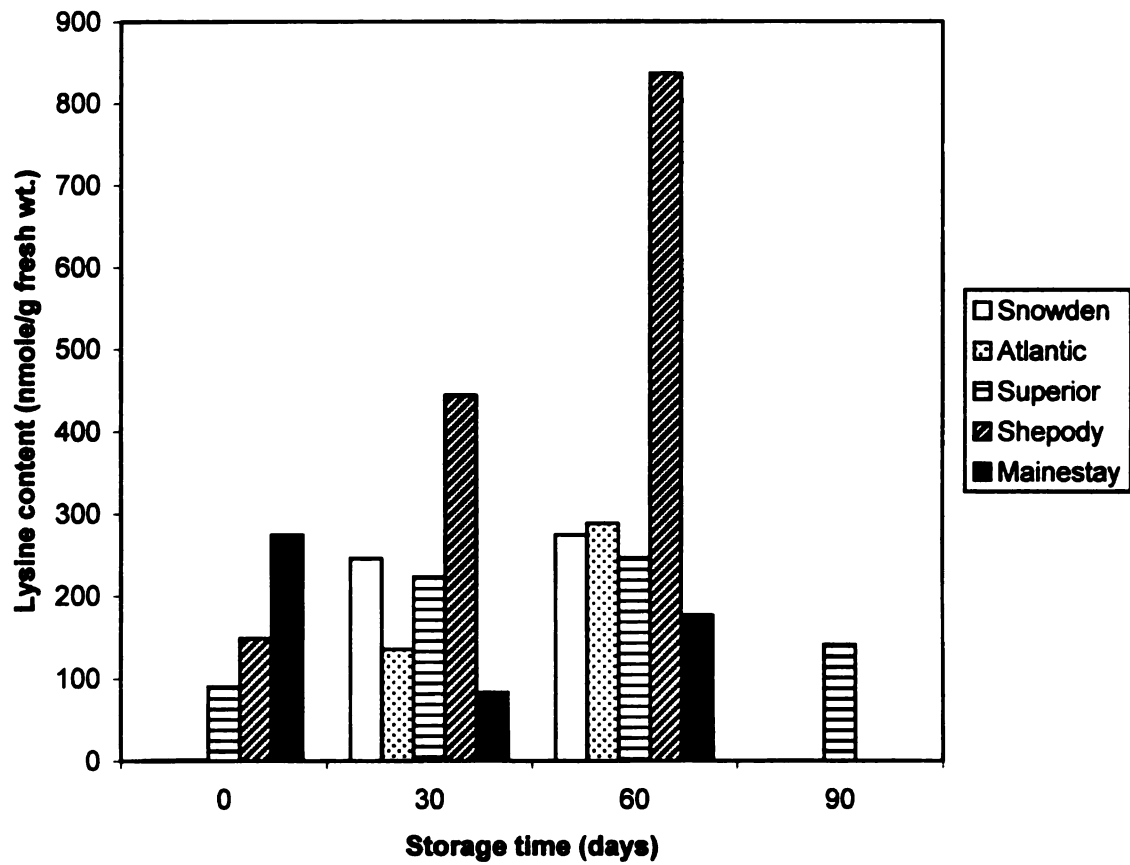


Figure 25. Lysine content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1995, at 0, 30, 60, and 90 days of storage.

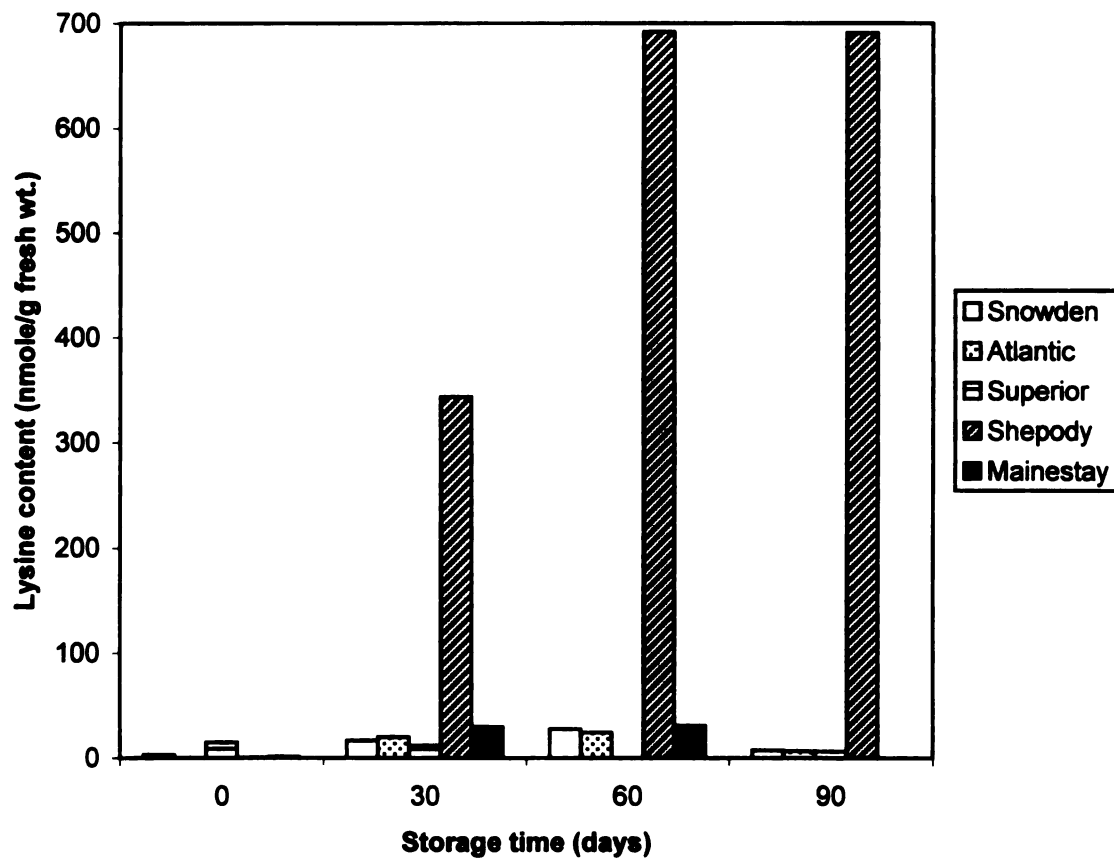


Figure 26. Lysine content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1996, at 0, 30, 60, and 90 days of storage.

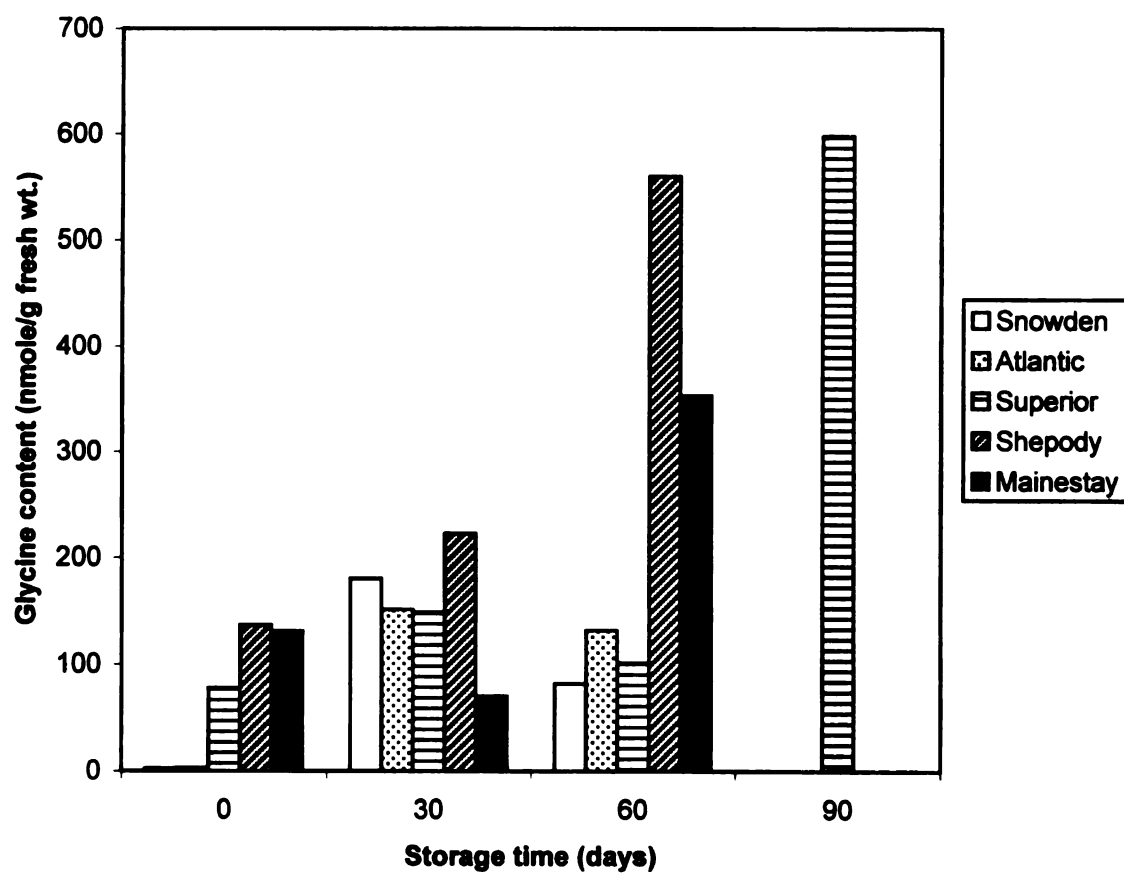


Figure 27. Glycine content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1995, at 0, 30, 60, and 90 days of storage.

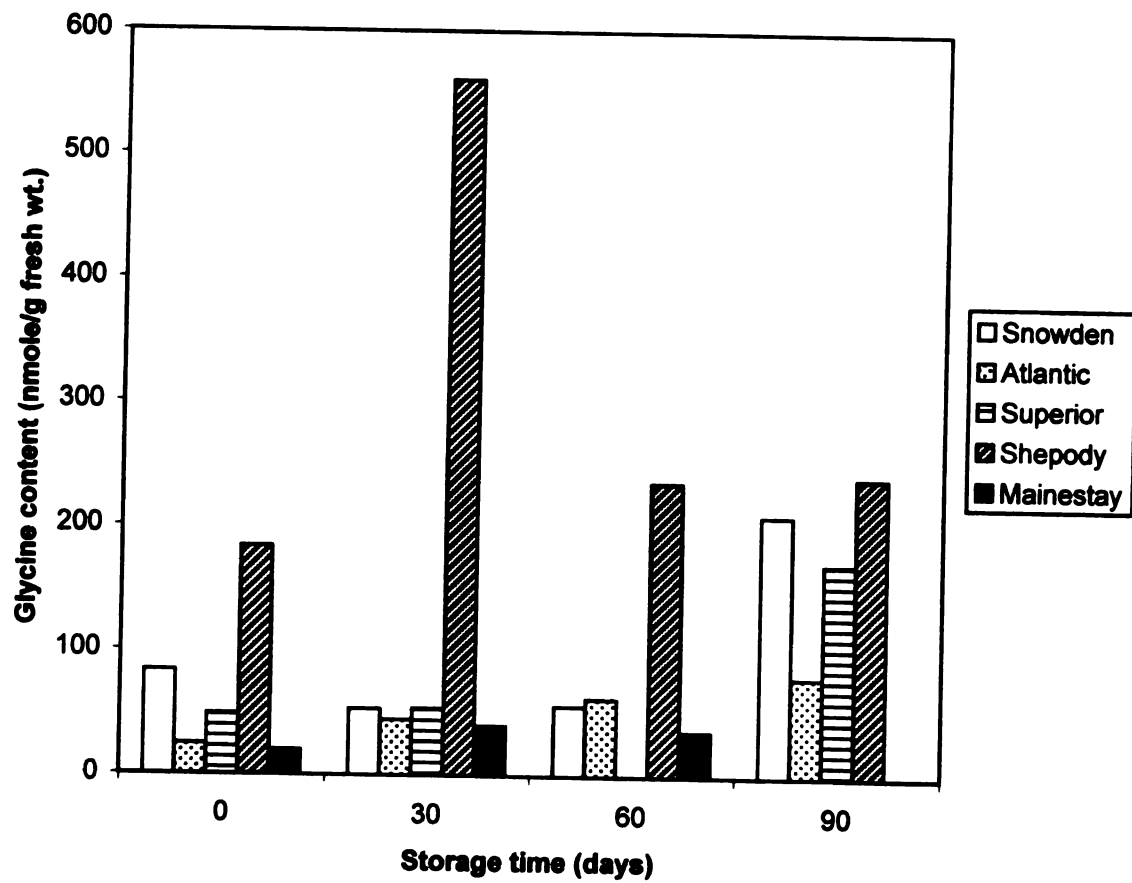


Figure 28. Glycine content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1996, at 0, 30, 60, and 90 days of storage.

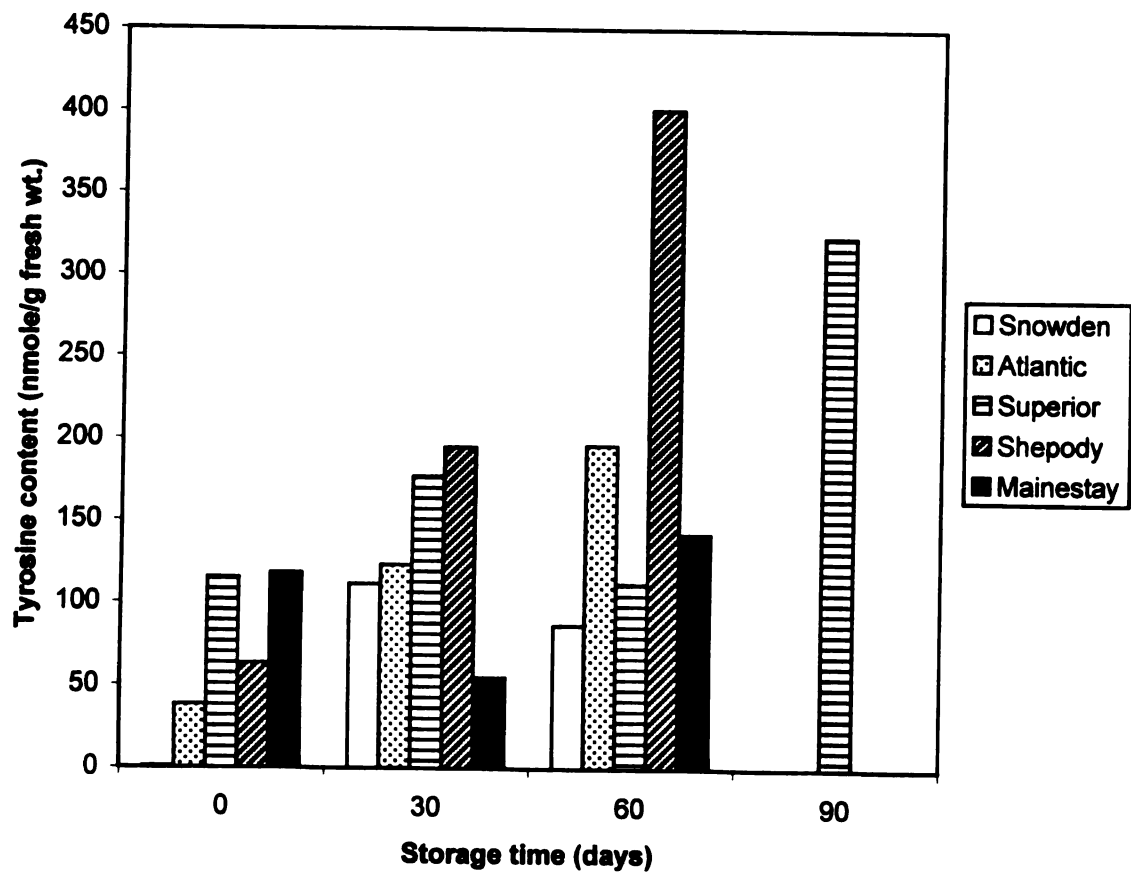


Figure 29. Tyrosine content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1995, at 0, 30, 60, and 90 days of storage.

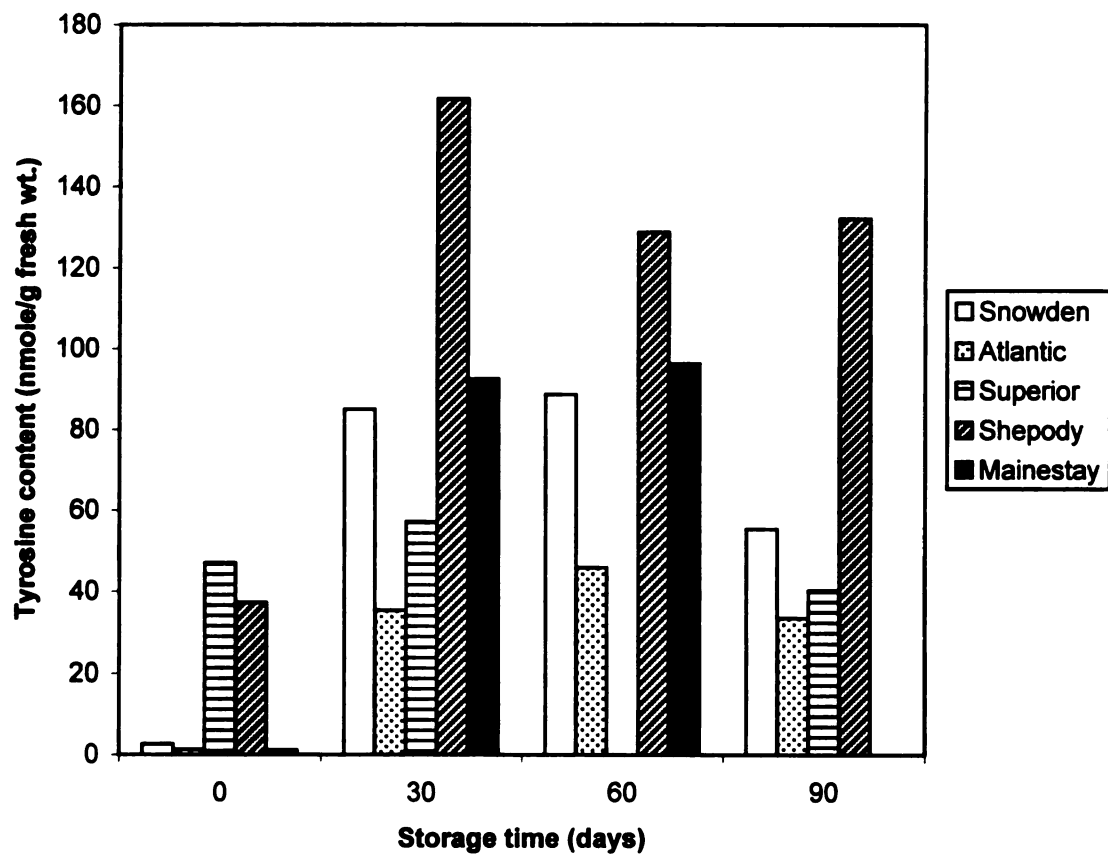


Figure 30. Tyrosine content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1996, at 0, 30, 60, and 90 days of storage.

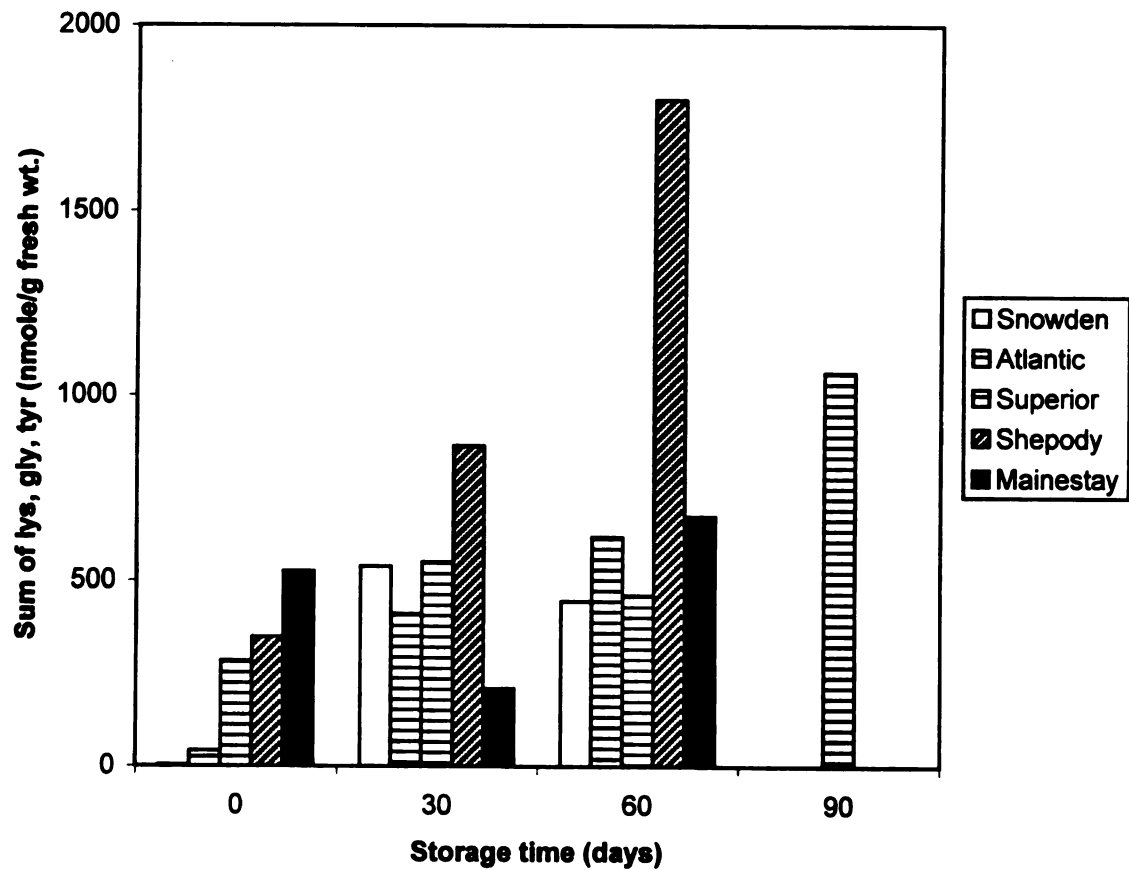


Figure 31. Sum of lys, gly, and tyr content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1995, at 0, 30, 60, and 90 days of storage.

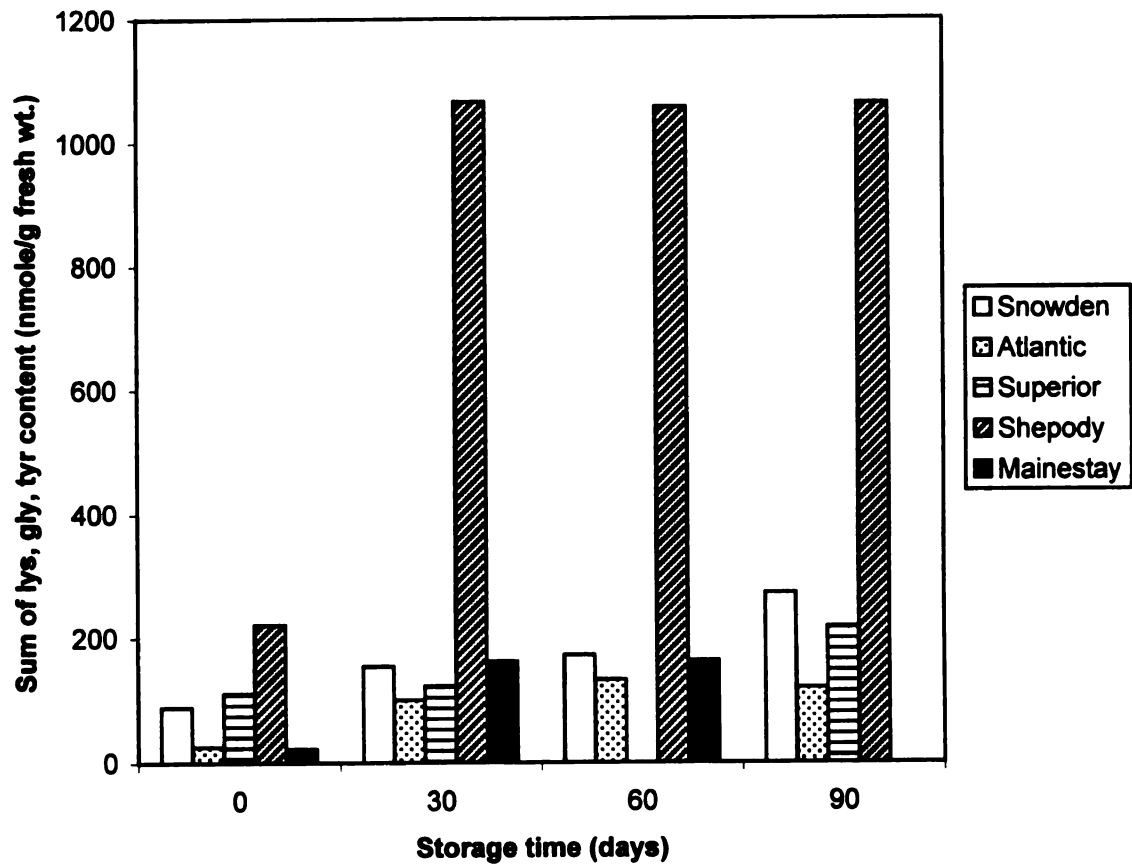


Figure 32. Sum of lys, gly, and tyr content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1996, at 0, 30, 60, and 90 days of storage.

For Snowden2 and the 4 selections, their lysine, glycine, tyrosine and sum of high browning producing amino acid contents during storage are shown in Figures 33 to 36, respectively. The results showed that chip color was poorly correlated with either lysine or glycine or tyrosine or total amounts of these amino acids. Similarly to Mainstay, these selections contained only low amounts of glucose hence the amount of high browning producing amino acids is not significant in chip color formation.

Free amino group content

Since the Maillard reaction involves the reaction between the free amino group present in natural protein and amino compounds, and the carbonyl group in reducing sugars, free amino group content is thought to be one of the critical factors in color development in potato chips.

Table 10 shows the free amino group contents of cultivars, Atlantic, Mainstay, Shepody, Snowden, and Superior, harvested in 1995 and 1996 at different storage times. The results showed that free amino group content generally increased over the storage period (Figures 37 and 38). Free amino acid and free amino group contents in tubers were in good agreement in terms of order. In general, Snowden and Atlantic contained the lowest amounts

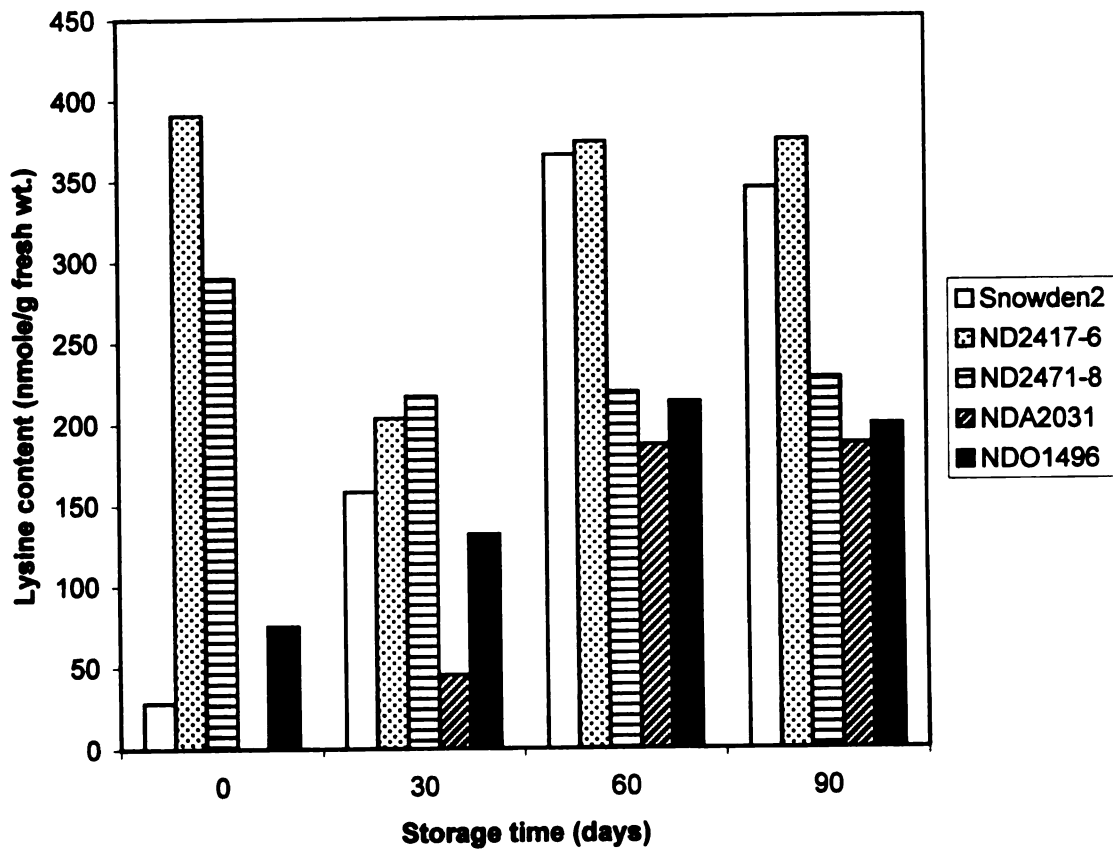


Figure 33. Lysine content of Snowden2, and selections, ND2417-6, ND2471-8, NDA2031, and NDO1496, harvested in 1996, at 0, 30, 60, and 90 days of storage.

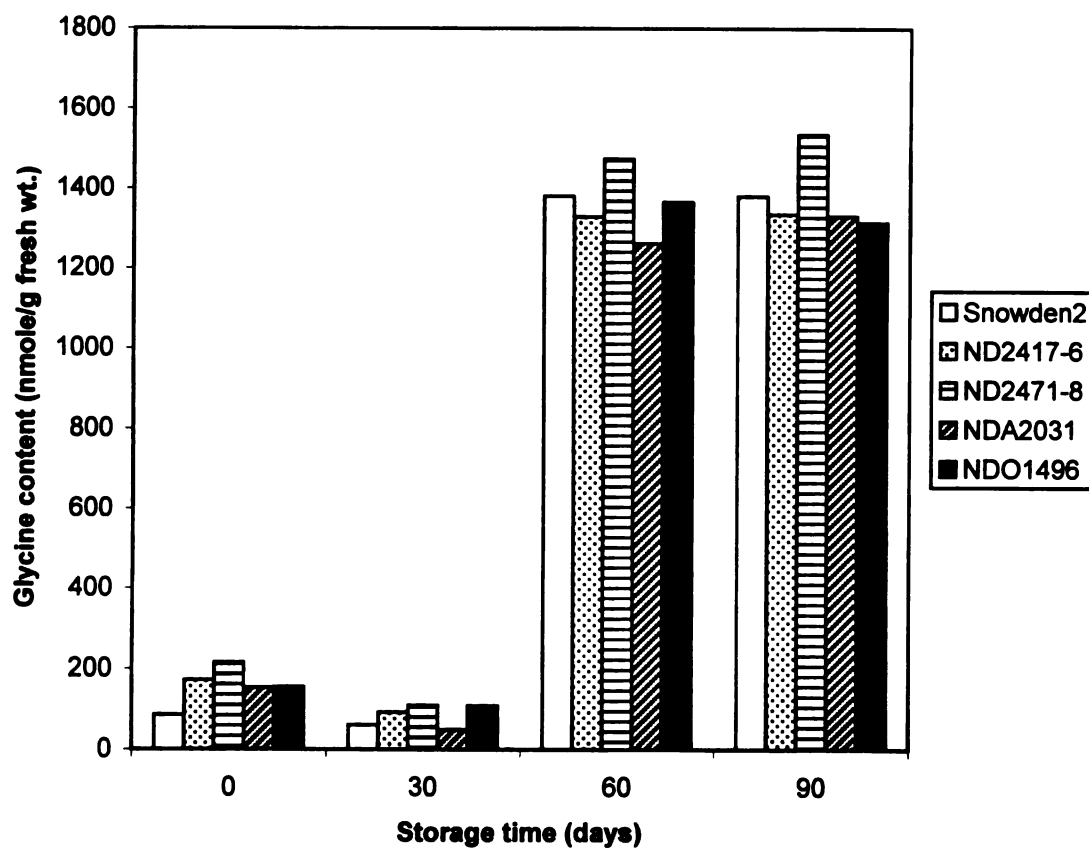


Figure 34. Glycine content of Snowden2, and selections, ND2417-6, ND2471-8, NDA2031, and NDO1496, harvested in 1996, at 0, 30, 60, and 90 days of storage.

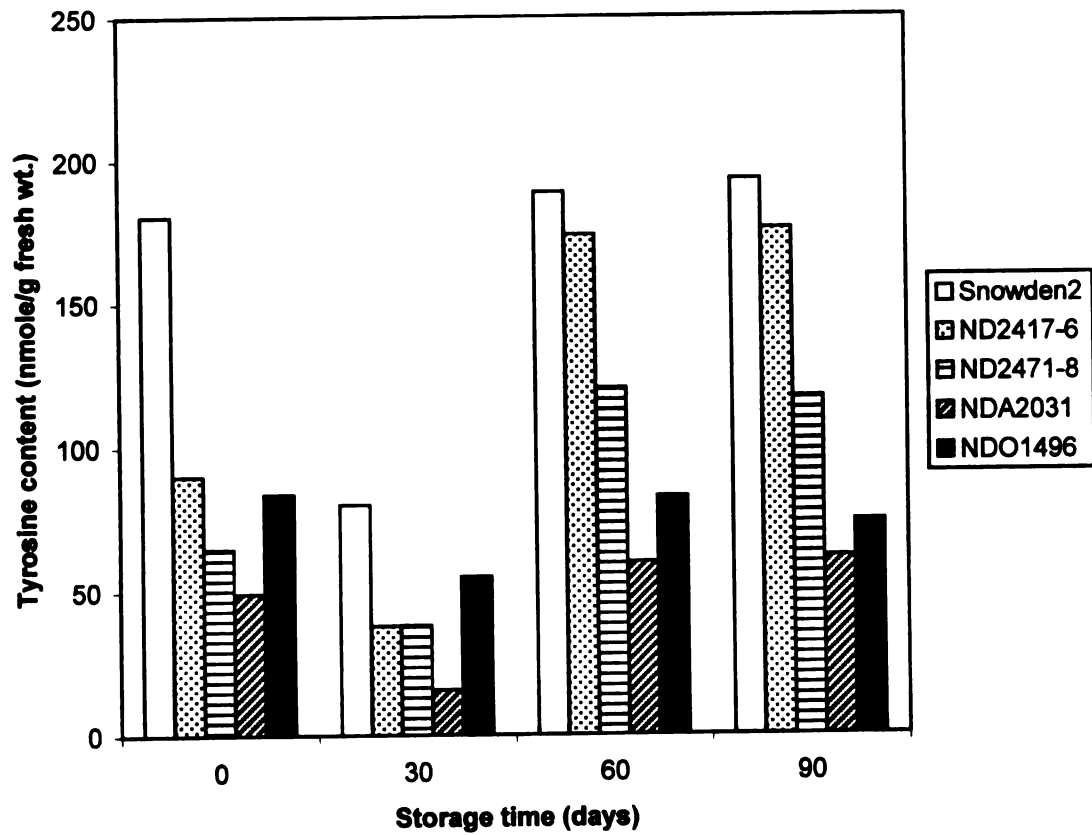


Figure 35. Tyrosine content of Snowden2, and selections, ND2417-6, ND2471-8, NDA2031, and NDO1496, harvested in 1996, at 0, 30, 60, and 90 days of storage.

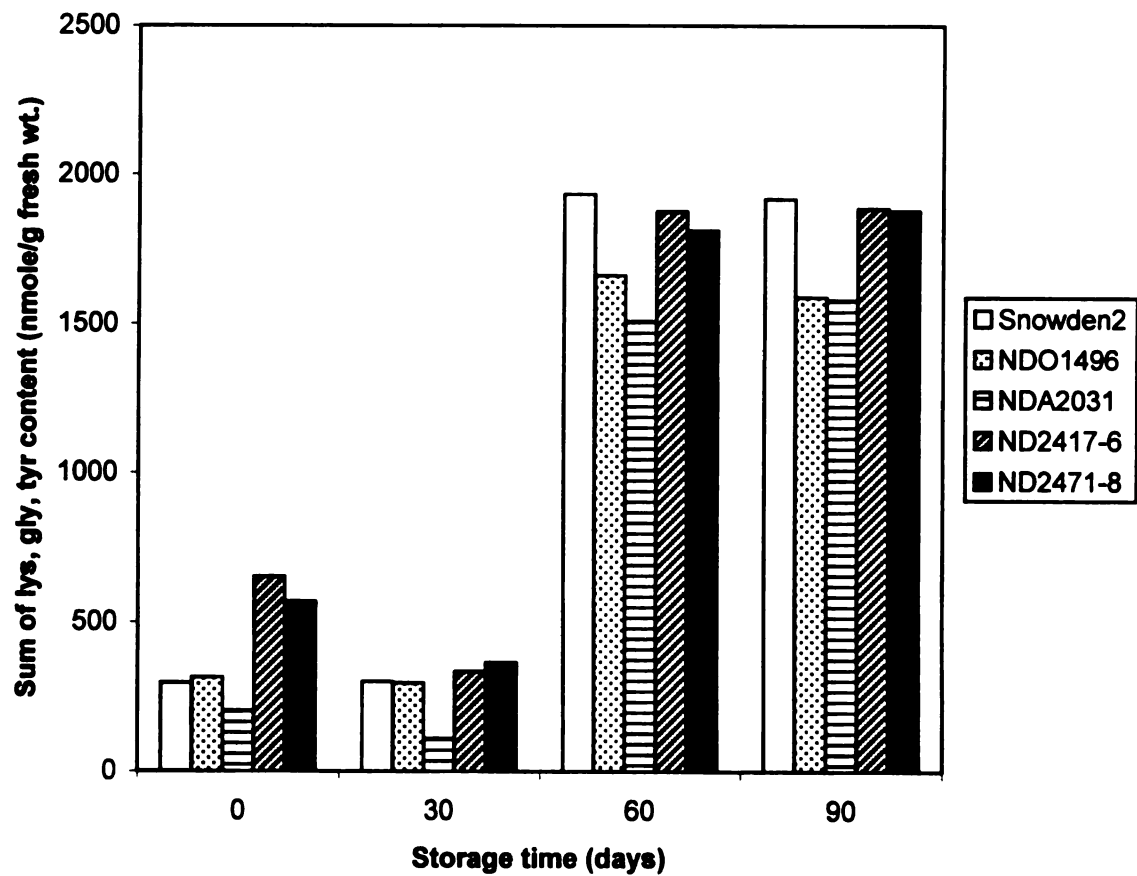


Figure 36. Sum of lys, gly, and tyr content of Snowden2, and selections, ND2417-6, ND2471-8, NDA2031, and NDO1496, harvested in 1996, at 0, 30, 60, and 90 days of storage.

Table 10. Free amino group content ($\mu\text{mole/g}$ fresh weight) and chip color of 5 potato cultivars, harvested in 1995 and 1996, at 0, 30, 60, and 90 days of storage.

Cultivar ¹	Storage time (days)	1995		1996	
		[NH ₂] ² ($\mu\text{mole/g}$)	Agtron no. ³	[NH ₂] ($\mu\text{mole/g}$)	Agtron no.
Snowden	0	1.20	66.2	1.40	63.3
	30	1.35	64.3	1.50	56.4
	60	2.29	61.1	1.60	56.2
	90	2.85	56.3	1.94	56.3
Atlantic	0	1.32	64.4	1.30	60.0
	30	1.42	63.0	1.17	58.8
	60	2.45	60.7	1.39	56.5
	90	3.08	55.8	1.61	55.4
Superior	0	1.94	57.9	1.69	57.9
	30	2.10	55.8	1.76	51.7
	60	2.81	51.9	1.92	50.8
	90	3.15	50.7	2.05	49.3
Shepody	0	3.23	50.5	1.79	55.8
	30	4.22	48.6	1.59	51.1
	60	4.84	44.3	1.97	50.1
	90	4.76	42.4	N/A	49.2
Mainstay	0	2.32	42.5	1.02	59.7
	30	2.71	42.0	1.48	52.3
	60	2.89	39.6	1.85	47.0
	90	N/A	N/A	2.17	41.6

¹ In order of decreasing average chip color.

² Free amino group content (average of two determinations) in $\mu\text{mole/g}$ fresh weight, using Ninhydrin assay.

³ Agtron number (average of 3 readings) > 60 = excellent;
56-60 = acceptable; 50-55 = marginally; < 45 = unacceptable.

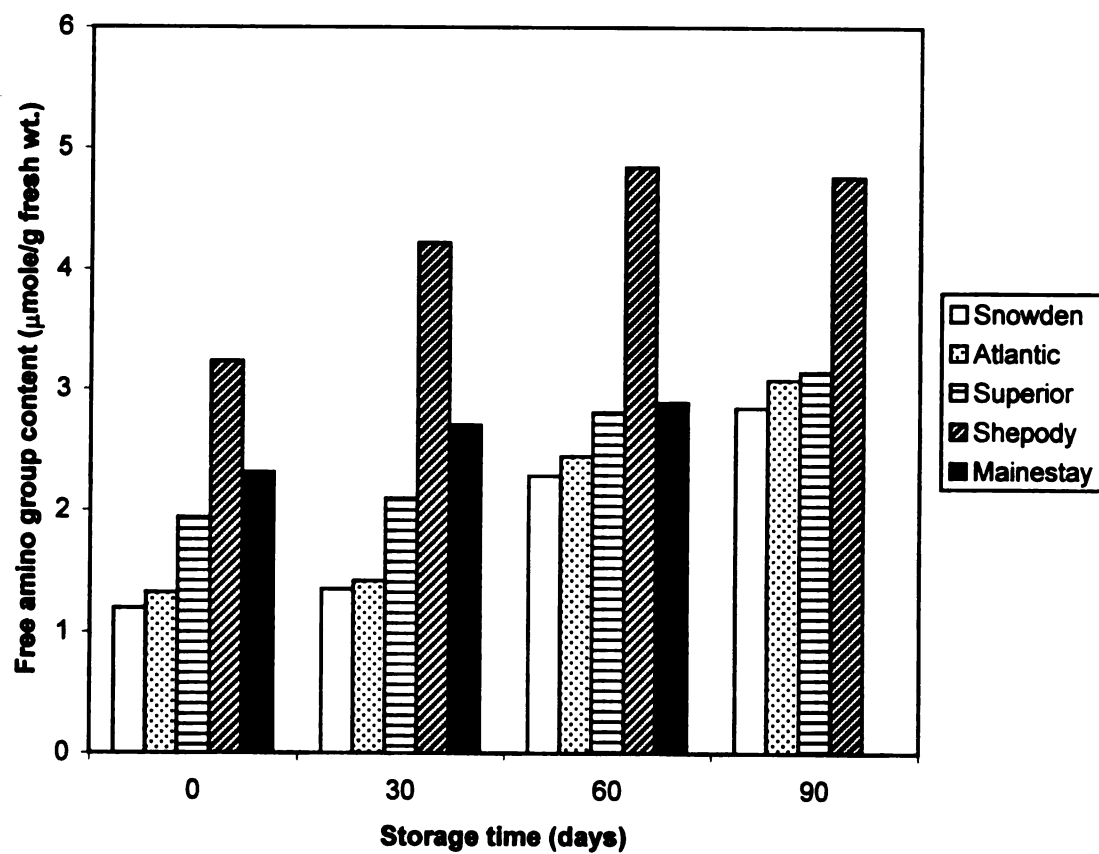


Figure 37. Free amino group content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1995, at 0, 30, 60, and 90 days of storage.

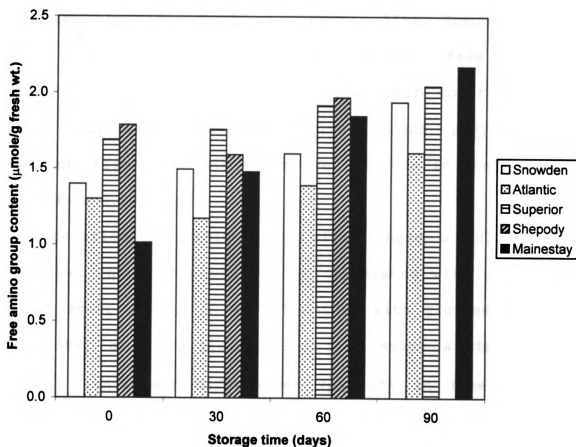


Figure 38. Free amino group content of cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1996, at 0, 30, 60, and 90 days of storage.

of free amino group and produced the most acceptable chips. Maiestay apparently contained high amounts of free amino groups, and glucose, and generally produced unacceptable chips. Shepody and Superior contained glucose within the same range. In 1995, Shepody generally contained the highest amounts of free amino groups and produced less acceptable chips than Superior. But in 1996, Shepody and Superior contained similar amounts of both free amino groups and glucose and produced similar chip color. The results indicated that free amino groups play more significant effect on chip color over glucose in the cases of Shepody and Superior.

Correlation coefficient data from these 5 cultivars showed that chip color was better correlated with glucose and free amino groups ($R = 0.94$), than with glucose alone ($r = 0.895$) or with glucose and free amino acids ($R = 0.930$). Significant differences ($p \leq 0.05$) in free amino group content were due to the effects of cultivar (Table A1). Storage time and the interactive effect of cultivar x storage time on free amino group content were not significant ($p \geq 0.05$).

Free amino group contents of Snowden2 and the selections, ND2417-6, ND2471-8, NDA2031, and NDO1496 are shown in Table 11 and Figure 39. Snowden2 and the

Table 11. Free amino group content ($\mu\text{mole/g}$ fresh weight) and chip color of Snowden2 and 4 selections, harvested in 1996, at 0, 30, 60, and 90 days of storage.

Cultivar ¹	Storage time (days)	[NH ₂] ² ($\mu\text{mole/g}$)	Agtron no. ³
Snowden2	0	1.18	62.0
	30	1.21	56.6
	60	1.53	54.7
	90	1.41	58.7
NDO1496	0	1.26	56.7
	30	1.46	53.8
	60	1.37	56.2
	90	1.20	57.6
NDA2031	0	1.06	56.0
	30	0.78	55.5
	60	1.40	55.9
	90	1.43	58.3
ND2417-6	0	1.00	55.0
	30	0.85	59.5
	60	1.24	57.3
	90	1.50	56.4
ND2471-8	0	1.46	54.6
	30	1.70	52.5
	60	1.57	52.4
	90	1.47	52.1

¹ In order of decreasing average chip color.

² Free amino group content (average of two determinations) in $\mu\text{mole/g}$ fresh weight, using Ninhydrin assay.

³ Agtron number (average of 3 readings) > 60 = excellent; 56-60 = acceptable; 50-55 = marginally; < 45 = unacceptable.

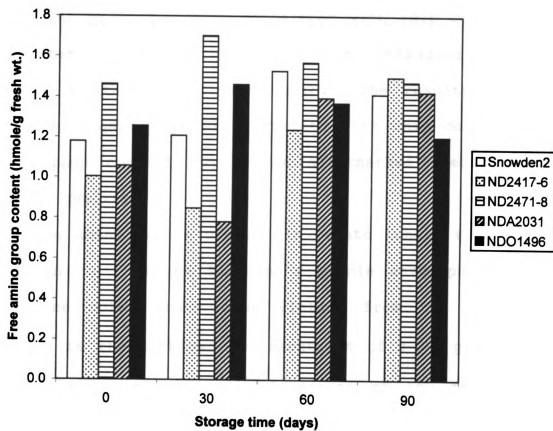


Figure 39. Free amino group content of Snowden2, and selections, ND2417-6, ND2471-8, NDA2031, and NDO1496, harvested in 1996, at 0, 30, 60, and 90 days of storage.

selections contained low amounts of free amino groups. Among these selections, ND2471-8 contained the highest amounts of free amino groups and produced the darkest chips. Significant effects ($p \leq 0.01$) of cultivar, storage time, and their interaction on free amino group content were observed for Snowden2 and these selections (Table A1). Free amino group was best correlated with chip color ($r = 0.53$) when compared with other factors including glucose, sucrose, or total free amino acid. The results suggest that when sugar is poorly correlated with chip color, free amino group content may be an alternative predictor of chipping quality.

Free amino groups present in potato tubers react with ninhydrin to form the Ruhemann's purple chromophore. It should be noted that color yielded from the ninhydrin reaction is the combined contributions of ϵ -NH₂ groups, N-terminal α -NH₂ groups, and NH₂ groups of any free amino acids. These free amino groups can participate in the Maillard reaction, and contribute to chip color. Free amino acids and the amides glutamine and asparagine contribute most of the non-protein nitrogen fraction in potato tubers. In addition to most of the common amino compounds, other compounds that can react with ninhydrin

include diamino acids, primary amines, peptides, proteins (Pearce et al., 1988), beta-alanine, gamma-aminobutyric acid, ornithine, homoserine (Leszkowiat et al., 1991), urea, and ammonia. However, free amino acids has been reported to range from 60-75% of the total free nitrogen in potato tubers (Kapoor et al., 1975). Therefore, the primary sources of free amino groups involving the Maillard reaction are amino acids. Although in a lesser extent than amino acids, non-amino acid compounds containing free amino groups play a role in chip color by entering the Maillard reaction. Free amino acid content determined by HPLC does not include non-amino acid nitrogen compounds present in tubers. Thus the free amino acid content is expected to be lower than the free amino group content. However, unexpected results were observed, as free amino group content was lower than free amino acid content in most cultivars at most storage times. It may be due to the fact that free amino acids contribute most of the free nitrogen in potato tubers. In addition, differences in color yields of amino acids and peptides occur when reacting with ninhydrin, presumably due to slow or incomplete reaction, or the formation of by-product (Pearce et al., 1988). Another possible cause of the unexpected results is the presence of other components in the systems, which may

interfere the reaction of some amino compounds with ninhydrin.

Correlation coefficients and coefficients of determination of the single regression are shown in Table 12 for cultivars, Atlantic, Mainstay, Shepody, Snowden, and Superior. The statistical results revealed that glucose was best correlated with chip color ($r = 0.90$), followed respectively by free amino groups ($r = 0.73$), free amino acids ($r = 0.47$), and sucrose ($r = 0.13$). However, general relationship between glucose and chip color was inconsistent. When combining values for either free amino acids, or free amino groups with glucose the correlation coefficients increased from $r = 0.90$ to $R = 0.93$, 0.94 , respectively. Therefore, free amino acids and free amino groups happened to be the factors affecting the relationship between glucose and chip color, suggesting that prediction of chip color can be improved by combining these factors with glucose. The results also suggest that free amino groups seemed to be more important in contributing to chip color than free amino acids. The highest correlation coefficients were observed ($R = 0.97$) when combining all factors (sucrose, free amino acid, and free amino group contents) with glucose.

Table 12. Correlation coefficients (R), coefficients of determination (R^2), and regression line for cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1995 and 1996.

Factors	R	R^2	Regression line ²
Color ¹ vs Glucose	0.895	0.800	C = 64.59-21.37G
Color vs Sucrose	0.133	0.018	C = 50.2+4.4S
Color vs Free amino acid	0.467	0.218	C = 59.37-0.002A
Color vs NH ₂ group	0.726	0.528	C = 69.18-5.82N
Color vs Glucose, Sucrose	0.898	0.806	C = 62.54-21.26G+2.59S
Color vs Glucose, Free amino acid	0.930	0.864	C = 67.56-21.73G-5.87A
Color vs Glc, NH ₂ group	0.942	0.888	C = 69.81-16.94G-2.8N
Color vs Glucose, Free amino acid, NH ₂ group	0.954	0.910	C = 72.09-18.07G-0.0007A-4.32N
Color vs Glucose, Sucrose, Free amino acid, NH ₂ group	0.970	0.941	C = 66.15-17.29G+7.01S+0.0002A-3.55N

¹ Chip color measured as Agtron number: > 60 = excellent; 56-60 = acceptable; 50-55 = marginally acceptable; < 45 = unacceptable.

² Abbreviations: A = free amino acid, C = chip color, G = glucose, N = free amino group, S = Sucrose.

For Snowden2 and the 4 selections, correlation coefficients and coefficients of determination of the single and multiple regression are shown in Table 13. The relationship between glucose and chip color can be improved by combining free amino groups or sucrose with glucose. In this case, multiple regression analysis including values for free amino acids did not improve the prediction of chip color. This supports the previous suggestion that free amino groups seems to be a better predictor for chip color than free amino acids. Similarly to the previous cases, the best correlation was found when combining values for free amino acids, free amino groups, and sucrose with glucose ($R = 0.59$).

Table 12 and Table 13 also report the regression line for the relationships with chip color. According to the correlation coefficients and the coefficients of determination, the suggested regression equation is expressed as:

$$C = 66.15 - 17.29 + 7.01S + 0.002A - 3.55N$$

Where:

A = free amino acid, C = chip color, G = glucose,

N = Free amino group, and S = sucrose.

Table 13. Correlation coefficients (R), coefficients of determination (R^2), and regression line for Snowden2 and selections, ND2417-6, ND2471-8, NDA2031, and NDO1496, harvested in 1996.

Factors	R	R^2	Regression line ²
Color ¹ vs Glucose	0.380	0.144	C = 57.78-22.09G
Color vs Sucrose	0.393	0.154	C = 59.93-6.37S
Color vs Free amino acid	0.075	0.006	C = 56.47-5.44A
Color vs NH ₂ group	0.467	0.218	C = 62.32-4.78N
Color vs Glucose, Sucrose	0.447	0.200	C = 59.83-14.28G-4.4S
Color vs Glucose, Free amino acid	0.380	0.144	C = 57.75-22.16G+4.35A
Color vs Glc, NH ₂ group	0.534	0.285	C = 62.51-15.71G-4N
Color vs Glucose, Free amino acid, NH ₂ group	0.583	0.340	C = 63.16-16.79G-0.0002A-5.51N
Color vs Glucose, Sucrose, Free amino acid, NH ₂ group	0.588	0.346	C = 63.52-14.33G-1.62S+0.0002A-5.12N

¹ Chip color measured as Agtron number: > 60 = excellent; 56-60 = acceptable; 50-55 = marginally acceptable; < 45 = unacceptable.

² Abbreviations: A = free amino acid, C = chip color, G = glucose, N = free amino group, S = Sucrose.

This relationship accounts for the highest degree of association (0.97 or 97%) from the data of 5 cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior.

From the glucose data accumulated in the present study, Figure 40 was constructed to show the use of glucose content in determining chipping acceptability. The glucose threshold of acceptability recommended by Sowokinos and Preston (1988) is 0.35 mg/g fresh weight. Chip color is acceptable at Agtron value higher than 45. The Plot shows that Atlantic, ND2417-6, ND2471-8, NDA2031, NDO1496, and Snowden, which are good chipping cultivars, generally contained glucose less than the safe value and produced acceptable chips. Mainestay generally contained glucose greater than the safe value and produced unacceptable chips.

Figure 41 shows the distribution of Agtron chip color of selected good chipping (Atlantic and Snowden) and poor chipping (Mainestay) cultivars. All of the chips produced from good chipping cultivars were acceptable or excellent. On the contrary, none of the chips made from poor chipping cultivar were excellent. The pie graph also shows that poor chipping cultivar consisted of high percentage of unacceptability (57%), but low percentage of acceptability (14%).

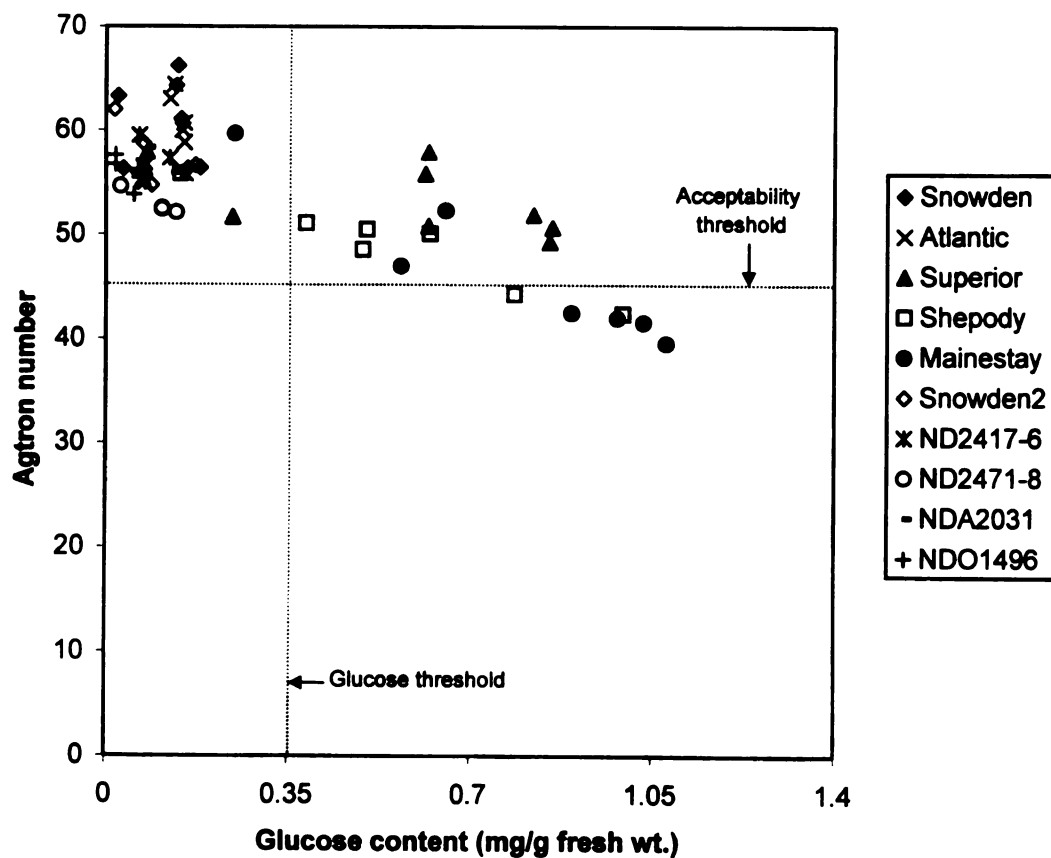


Figure 40. Glucose content and chip color of cultivars, Atlantic, Mainestay, Shepody, Snowden, Snowden2, Superior, and selections, ND2417-6, ND2471-8, NDA2031, and NDO1496, harvested in 1995 and 1996, at 0, 30, 60, and 90 days of storage.

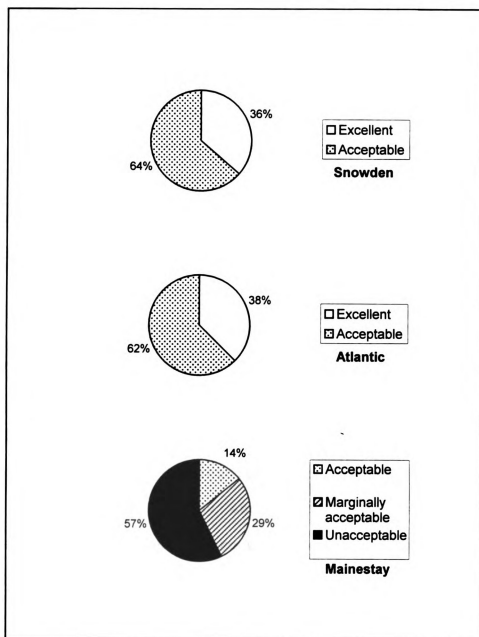


Figure 41. Distribution of Agtron chip color for selected good chipping cultivars (Snowden and Atlantic), and poor chipping cultivar (Mainstay) over 90 days of storage.

CONCLUSION

The effects of sugars, free amino acids, and free amino groups on chip color development were investigated. In most cases, glucose was well correlated with chip color. Snowden and Atlantic, which are good chipping cultivars, generally contained low amounts of sugars, free amino acids, and free amino groups. Mainstay, which is a poor chipping cultivar, generally contained the highest amounts of glucose and produced the darkest chips. In this case free amino acid and free amino group contents were not significant in contributing to chip color. Glucose content alone may not be used to regularly predict the fried color of chips made from Shepody and Superior. However, free amino acid and free amino group contents were found to be helpful in chip color prediction in Shepody and Superior.

Statistical results revealed that prediction of chip color can generally be improved by combining values of free amino acid and/or free amino group contents with sugar contents. The best correlation is a multiple regression combined all the factors (glucose, sucrose, free amino

acids, and free amino groups) with chip color. It was reported to improve the general relationship between chip color and glucose from 90% to 97%.

The new selections, which tend to possess good chipping performance, contained glucose less than 0.35 mg/g fresh weight and achieved an SR value below 1.0 throughout the storage period. All selections except ND2471-8 generally produced acceptable chips.

In most cases, the amounts of glucose in potatoes were of greater importance than amino acids and amino groups in chip color development. This is not surprising considering the three-to four fold molar excess of amino acids over sugars in potato tubers. Therefore, reducing sugars are the limiting factor in chip color development. Sugar level seems to be the most practical and reliable predictive test of the suitability of material for chipping.

Statistical results showed that free amino group content correlated with chip color better than free amino acids. It also correlated with chip color better than glucose for the data from Snowden2 and the selections. This suggested that in addition to sugar, free amino group content might be another important chemical factor contributing to chip color. Ninhydrin assay was developed to monitor free amino group content of potatoes at harvest,

and in storage. This method is also useful in determining the accumulation of free amino acid after storage due to protein breakdown. As compared to the conventional amino acid analysis (HPLC), possible advantages of the ninhydrin assay are that it measures not only free amino acids, but also other related compounds containing free amino groups. In addition, ninhydrin assay is simpler and requires less expensive equipment as compared to amino acid analysis using HPLC. This assay merits further investigation as an applicable method for determining processing stability of potatoes in conjunction with sugar. Moreover, the information on free amino compounds accumulated in the present study may be helpful for future study towards development of varieties that accumulate low reducing sugars, total free amino acids, and high browning producing amino acids (e.g. lysine, glycine, and tyrosine).

Storage duration showed an effect on free amino acid content. The accumulation of free amino acids during storage may be another factor influencing processing quality of potato chips since free amino acids involve in the Maillard browning reaction. Future research could study the effect of different periods of storage duration and storage temperature on free amino acid content of potatoes in relation to chip color. Reconditioning process

may also be conducted to investigate if it is an effective mean in lowering the free amino acid pool size as in sugar.

Due to variable ratios and amounts of sugars and amino acids among different potato cultivars, future research is required to accumulate more data on color development in potato chips made from other cultivars. A number of good and poor chipping cultivars may be evaluated in terms of sugars, free amino acids, and free amino groups to determine their association to chip color. Other specific amino acids may significantly contribute to chip color.

APPENDIX

Table A1. Analysis of variance for glucose, sucrose, free amino acid, and free amino group contents of potato tubers.

Source	df	Mean Squares ¹			
		Glucose	Sucrose	Free amino acid	Free amino group
<u>5 cultivars²</u>					
Cultivars	4	0.77**	0.02	23780331**	2.51*
Storages ³	3	0.16*	0.11	14127567**	2.01
Cultivars x Storages	12	0.04	0.05	1583532	0.03
Error ⁴	20	0.04	0.070		0.86
	15			2051645	
<u>Snowden2 and selections⁵</u>					
Cultivars	4	0.004*	0.14**	29964512**	7.46**
Storages ³	3	0.008*	0.004**	41190575**	6.02**
Cultivars x Storages	12	0.002*	0.026**	450816*	0.14**
Error	20	0.0018	4.40E-16	243953	0.69

¹ n=2, *=significant at $P \leq 0.05$, **=significant at $P \leq 0.01$.

² Cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1995 and 1996.

³ Storages include: fresh harvest and after 30, 60, and 90 days.

⁴ 5 cases were missing for free amino acid, due to experimental error.

⁵ Snowden2 and selections, ND2417-6, ND2471-8, NDA2031, and ND01496, harvested in 1996

Table A2. Analysis of variance for high browning producing amino acid (lysine, glycine, and tyrosine) contents of potato tubers.

Source	df	Mean Squares ¹			Sum of lys, gly, tyr
		Lysine	Glycine	Tyrosine	
<u>5 cultivars²</u>					
Cultivars	4	121496**	63998**	9716	486568**
Storages ³	3	103376**	31783	22383*	421053**
Cultivars x Storages	12	41080*	6660	3675	98500
Error ⁴	15	16639	13021	4992	65014
<u>Snowden2 and selections⁵</u>					
Cultivars	4	53736**	20841**	15496**	161787**
Storages ³	3	39036**	5228516**	14099**	6762337**
Cultivars x Storages	12	12322**	4349	1345**	16794**
Error	20	26	2226	39	2288

¹ n=2, *=significant at P ≤ 0.05, **=significant at P ≤ 0.01.

² Cultivars, Atlantic, Mainestay, Shepody, Snowden, and Superior, harvested in 1995 and 1996.

³ Storages include: fresh harvest and after 30, 60, and 90 days.

⁴ 5 cases were missing for the amino acids, due to experimental error.

⁵ Snowden2 and selections, ND2417-6, ND2471-8, NDA2031, and NDO1496, harvested in 1996

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