REVIEWS

Chemistry, Biochemistry, and Dietary Role of Potato Polyphenols. A Review

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Potatoes and other plant foods accumulate a variety of secondary metabolites, including phenolic compounds, phytoalexins, protease inhibitors, and glycoalkaloids, as a protection against adverse effects of mechanical bruising, light, and injury by predators including beetles, fungi, and insects. Since these phytochemicals are consumed by insects, animals, and humans as part of their normal diet, a need exists to develop a better understanding of the role of these compounds in both the plant and the diet. To contribute to this effort, this multidisciplinary overview describes analytical and compositional aspects of phenolic compounds in potatoes; their biosynthesis, molecular genetics, and role in host-plant resistance relationships; bruising-, ferrous ion-, and heat-induced discolorations such as after-cooking blackening and blackspot formation, which affect appearance and sensory properties of potatoes; polyphenol-oxidase-catalyzed enzymatic browning reactions and their prevention by chemical and plant molecular biology techniques; and effects of baking, cooking, microwaving, light, and γ-radiation on the stability of the major potato polyphenol, chlorogenic acid. Also covered are beneficial effects of phenolic compounds in the diet as antioxidants, antimutagens, anticarcinogens, antiglycemic, and hypocholesterolemic agents; adverse effects on protein nutritional quality; and recommendations for future research. Understanding the biochemical basis of stress-induced formation of polyphenols in plants, the chemistry of their transformations in the plant and in foods, and their functions in plant physiology, food science, nutrition, and health should stimulate interest in maximizing beneficial sensory, nutritional, and health effects of polyphenols in the diet. Such efforts should lead to better foods and improved human health.

Keywords: *Antioxidant; blackspot; browning; browning prevention; chlorogenic acid; food quality; food safety; glycoalkaloids; health; host-plant resistance; nutrition; plant genetics; plant physiology; polyphenol oxidase; polyphenols; potatoes; γ-radiation; Solanum tuberosum; storage*

INTRODUCTION

Polyphenolic compounds are secondary plant metabolites found in numerous plant species, including potatoes (Deshpande et al., 1984). The oxidation products of phenolic compounds appear to be involved in the defense of plants against invading pathogens, including bacteria, fungi, and viruses. Polymeric polyphenolic compunds seem to be more toxic to potential phytopathogens than are the phenolic monomers, such as chlorogenic acid, from which they are derived. The polyphenol-oxidase-catalyzed polymerization helps seal the injured plant surface and begins the healing process, analogous to the formation of fibrin blood clots in injured humans.

Enzyme-catalyzed browning reactions (Hurrell and Finot, 1984; Lee and Whitaker, 1995; Schwimmer, 1981) involve the oxidation of phenolic compounds by the enzyme tyrosinase (polyphenol oxidase, PPO) to quinones, followed by transformation of the quinones to dark pigments. These result in deterioration of flavor, color, and nutritional quality and continue after the food is harvested. Therefore, prevention of enzymatic browning in fruits and vegetables has been a major concern of food scientists.

Polyphenolic compounds have also been shown to possess antimutagenic, anticarcinogenic, antiglycemic, and antioxidative beneficial properties. These properties can be utilized in the prevention of rancidity and in the development of health-promoting food ingredients. They may also adversely affect protein nutritional quality.

To cross-fertilize information among several disciplines (including plant science, entomology, food science, nutrition, and medicine) interested in plant phenolics, I have attempted to integrate and correlate the widely scattered literature on the role of potato polyphenols during plant development and growth and after harvest. Specifically covered are the following relevant aspects: analysis; composition; biosynthesis; host-plant resistance; chemistry of enzymatic browning, blackspots, and other discolorations; heat-, light-, and γ-radiation-induced changes; pre- and postharvest browning prevention; and beneficial effects following consumption. Suggestions for future research are also mentioned to catalyze progress in minimizing the adverse effects of potato polyphenols and enhancing the desirable ones.

Since chlorogenic acid constitutes up to 90% of the total phenolic content of potato tubers, most of the discussion centers around this compound. Figure 1 shows the structures of potato phenolics, including chlorogenic acid and its isomers.

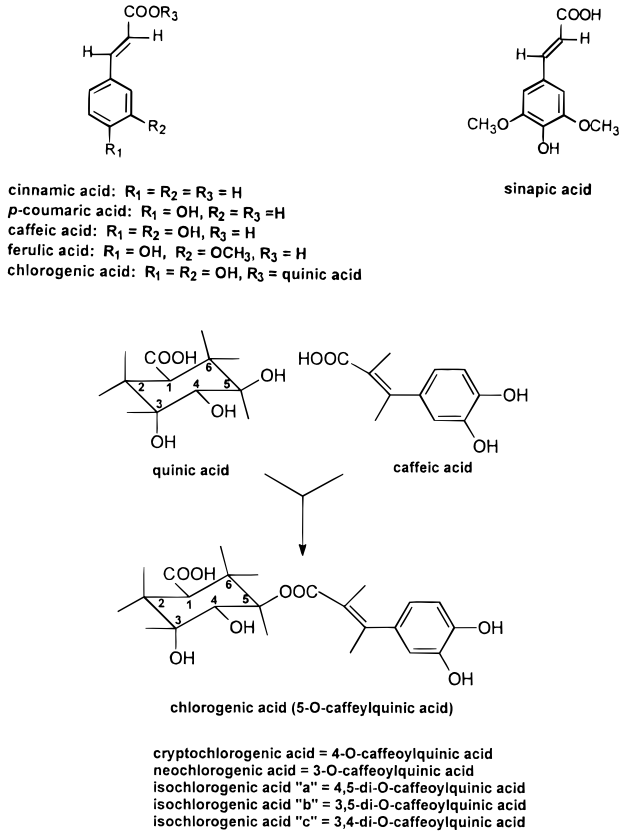

Figure 1. Structures of potato polyphenols and chlorogenic acid isomers.

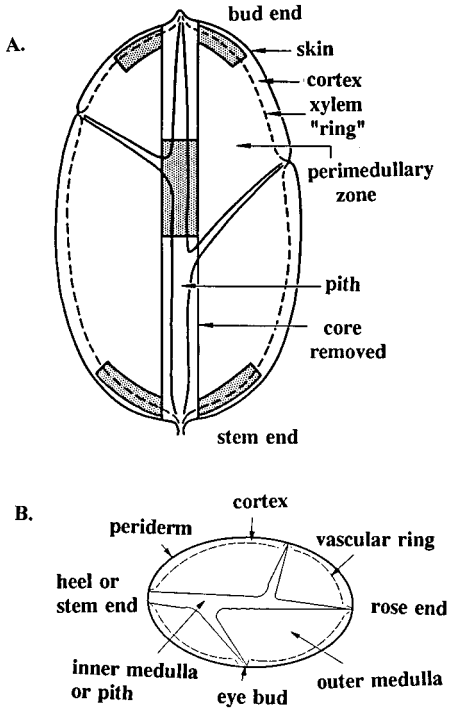

Figure 2. Cross section of a potato tuber: (A) Reeve et al. (1969); (B) Olsson (1989).

ANALYSIS AND COMPOSITION

Current analytical methods for potato polyphenols include gas−liquid chromatography (GLC), high-performance liquid chromatography (HPLC), thin-layer chromatography (TLC), and UV spectrophotometry, but surprisingly, not immunoassays. Before analysis, the compounds have to be extracted and purified. Voigt and Noske (1964) describe optimized extraction of chlorogenic acid from potatoes with the aid of acetone, ethanol, and methanol. The order of effectiveness was methanol > ethanol > acetone. They found that the chlorogenic acid content of stewed potatoes was the same as that of raw potatoes.

Phenolic compounds are distributed mostly between the cortex and skin (peel) tissues of the potato (Reeve et al., 1969; Figure 2). About 50% of the phenolic compounds were located in the potato peel and adjoining tissues, while the remainder decreased in concentration from the outside toward the center of potato tubers (Hasegawa et al., 1966).

Several isomeric chlorogenic acids have been found in potatoes. The major one, now designated 5-caffeoylquinic acid by the International Union of Pure and Applied Chemistry (IUPAC), is complemented by 3- and 4-caffeoylquinic acids. The IUPAC numbering system differs from that used by Brandl and Herrman (1984). Whether all of these isomers occur naturally, or some are artifacts formed during extraction and isolation, is an unresolved issue (Molgaard and Ravn, 1988).

Tisza et al. (1996) used a new GC-MS method for the quantitation of chlorogenic, citric, malic, and caffeic acids and of fructose, glucose, and sucrose in freeze-dried potato samples. The chlorogenic acid content of freeze-dried potato tubers, but not sprouts, correlated with values obtained by UV spectroscopy.

Brandl and Herrmann (1984) and Nagels et al. (1980) describe HPLC separation of chlorogenic acid isomers in potatoes. Different potato cultivars grown under the same conditions contained the following isomers: 3-*O*-caffeoylquinic (*n*-chlorogenic acid), 4-*O*-caffeoylquinic (*crypto*-chlorogenic acid), 5-*O*-caffeoylquinic (*neo*-chlorogenic acid), 3,4-dicaffeoylquinic, and 3,5-dicaffeoylquinic.

Boussenadji et al. (1993) developed a liquid chromatographic technique with electrochemical detection to measure electroactive antioxidative polyphenols added to foods and drugs to inhibit their oxidation. Related studies from this laboratory describe HPLC of glycoalkaloids with pulsed amperometric detection (Friedman and Levin, 1995; Friedman et al., 1994). Electrochemical detection methods may therefore be useful in the analysis of potato glycoalkaloids and polyphenols.

Griffiths et al. (1992) describe a colorimetric method for measuring chlorogenic acid in freeze-dried potato tubers based on the reaction of the acid with nitrous acid. Application of this method to 13 potato cultivars revealed that, in most cases, the chlorogenic acid content of the stolon end of tubers could be related to the susceptibility to after-cooking-blackening. However, in two genetically related cultivars, the amount of blackening was greater than would be predicted solely on the basis of chlorogenic acid content.

Spectrophotometric analysis of potato chlorogenic acid gave higher values than did analysis by HPLC or GLC (Malmberg and Theander, 1985). Spectrophotometry may give high values because chlorogenic acid isomers contribute to the total absorbance. Since GLC requires derivatization, HPLC may be preferable as a general method. However, HPLC analysis may not always be satisfactory because chlorogenic acid undergoes a time- and light-dependent change.

Because of this unexpected problem we encountered with the HPLC method (Dao and Friedman, 1992, 1994; Friedman and Dao, 1990; Friedman et al., 1989), we evaluated the effectiveness of a UV method for measuring chlorogenic acid in several varieties of fresh potatoes as well as in parts of the potato plant, processed potato products, and weed seeds (Tables 1−4). Chlorogenic

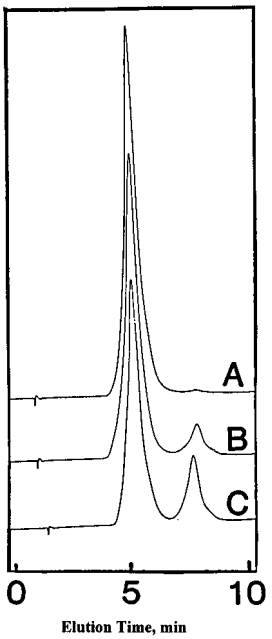

Figure 3. HPLC chromatogram of chlorogenic acid in methanol: (A) freshly prepared; (B) after 1 day; and (C) after 7 days (Dao and Friedman, 1992).

Table 1. Chlorogenic Acid Content (Milligrams per 100 g of Fresh Weight) in Different Potato Varieties (Dao and Friedman, 1992, 1994)

variety	chlorogenic acid
Russet (small commercial)	9.65 ± 0.49
Russet (large commercial)	14.22 ± 0.73
small red (commercial)	13.30 ± 0.69
Simplot I (experimental)	13.14 ± 0.94
Simplot II(experimental)	17.36 ± 1.19
NDA 1725 (experimental)	17.36 ± 1.19
potato 3194 (experimental)	18.71 ± 2.10

Table 2. Distribution of Chlorogenic Acid (Milligrams per 100 g of Fresh Weight) in Parts of a Potato Plant (Dao and Friedman, 1992, 1994)

sample	chlorogenic acid	sample	chlorogenic acid
tubers	17.36 ± 1.19	leaves	223.53 ± 0.95
roots	26.34 ± 0.82	sprouts	754.06 ± 25.17

Table 3. Heat Stability of Chlorogenic Acid (Milligrams per Gram of Freeze-Dried Weight) in Cooked Potatoes Determined by UV Spectrophotometry (Dao and Friedman, 1992)

potato	chlorogenic acid	potato	chlorogenic acid
fresh	0.800 ± 0.05	boiled	0.319 ± 0.01
baked	0.000	microwaved	0.434 ± 0.02

Table 4. Stability of Chlorogenic Acid during Baking of Mixed Heavenly Blue Morning Glory and Wheat Flour (Friedman and Dao, 1990)

sample	% loss
unbaked mixed flour	0
convection oven baked muffin	
crust fraction	100
crumb fraction	65.1 ± 1.9
microwave oven baked muffin	77.0 ± 0.92

acid underwent a time- and light-dependent change in the methanolic and ethanolic extracts of potatoes (Figure 3). The decrease of the chlorogenic acid peak on chromatograms was accompanied by a corresponding increase of a new peak. Use of ultraviolet spectrophotometry to estimate chlorogenic acid was reproducible, apparently because the newly formed compound(s) had an absorption maximum similar to that of chlorogenic acid (Figure 4). Nearly all of the chlorogenic acid in

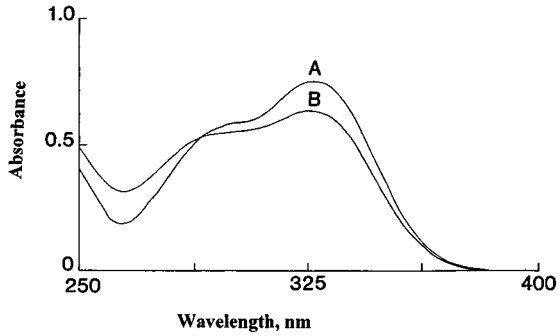

Figure 4. UV spectra of (A) chlorogenic acid and (B) an ethanol extract of potato roots (Dao and Friedman, 1992).

Table 5. Effect of Growing Time in a Greenhouse on Chlorogenic Acid Content [Milligrams per 100 g of Fresh Weight (n = 3)] of Freeze-Dried Potato Leaves Determined by UV Spectrophotometry (Dao and Friedman, Unpublished Results)

time (weeks)	chlorogenic acid	
	mean value	95% CI (coefficients of variation)
3	148.0	131.9, 164.1
4	152.1	135.9, 168.3
6	305.7	289.6, 321.9
7	423.1	406.9, 439.3
9	257.8	241.6, 274.0

spiked potato powders was recovered. Thus, the UV method may have advantages over HPLC. However, UV spectroscopy measures total content, while HPLC can measure specific polyphenols in a mixture. Thus, when HPLC is used, extracts of plant, food, and animal tissues should be analyzed immediately to minimize formation of new products that may coelute with known polyphenols on HPLC colunms. Generally, HPLC, UV, and GC-MS methods need to be further compared, correlated, and validated.

Using UV spectroscopy, we found that potatoes and potato plants contained an average of 754 mg/100 g of fresh weight for sprouts, 224 mg/100 g for leaves, 26 mg/100 g for roots, and 17 mg/100 g for tubers. Oven-baked potatoes contained no chlorogenic acid, boiled potatoes 35%, and microwaved potatoes 55% of the original amount. French fried potatoes, mashed potato flakes, and potato skins contained no chlorogenic acid. Leaves contained high levels of chlorogenic acid and glycoalkaloids (Dao and Friedman, 1996; Lyon and Barker, 1984; Table 5). Sosulski et al. (1982) report a total phenolic acid content of potato flour of 410 ppm, with free chlorogenic acid contributing 83.2% to the total. Figure 5 and Table 4 show changes in chlorogenic acid during baking.

Although potato processors are generally interested in imparting desirable sensory (organoleptic) attributes to potato products, the discovery of several beneficial effects of dietary phenolic compounds, described below, implies that food-processing conditions may need to be optimized to minimize destruction of chlorogenic acid while maintaining sensory quality. The fate of chlorogenic acid and other polyphenols during food processing is largely unknown. All such studies depend on reliable analytical methods for phenolic compounds; these are still being refined.

PLANT PHYSIOLOGY

Biosynthesis. Chlorogenic acid and related polyphenols are present in numerous plant species including those of the Solanaceae family (Deshpande et al., 1984). Their main function in plants appears to be to defend

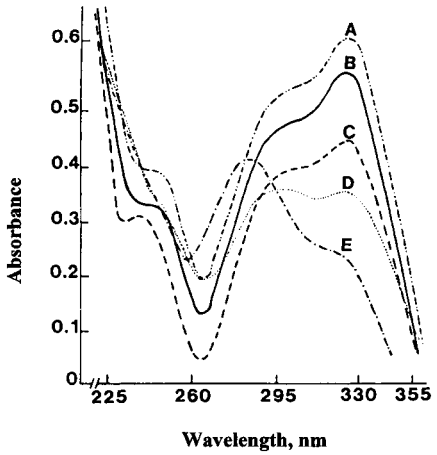

Figure 5. Effect of baking on the stability of chlorogenic acid measured by UV spectroscopy in a muffin prepared from a mixture of chlorogenic acid containing morning glory seed flour and wheat flour: (A) chlorogenic acid; (B) ethanolic extract of morning glory seeds; (C) ethanolic extract of crumb fraction of oven-baked muffin; (D) extract of microwave-baked muffin; and (E) extract of crust fraction of oven-baked muffin (Friedman and Dao, 1990).

against phytopathogens, as described below for potatoes. Biosynthetically, chlorogenic acid is derived from phenylalanine, which in turn is formed via the classical shikimate pathway starting from phosphoenol pyruvate and erythrose 4-phosphate, as described by Herrmann (1995) and Schmidt and Amrhein (1995). Figure 6 shows the biosynthetic transformations of phenylalanine to chlorogenic acid (Villegaas and Kojima, 1986). Chlorogenic acid biosynthesis has an absolute requirement for oxygen. Phenylalanine is also a precursor for flavonol biosynthesis in potatoes (van Eldik et al., 1997).

Detailed discussion of the enzymes involved in the illustrated biosynthetic transformations is beyond the scope of this paper. Useful descriptions can be found in Moriguchi et al. (1988) and Tanaka and Kojima (1991).

Ontario potatoes (which are very susceptible to precooking blackening) grown at high levels of potassium fertilization had higher cytochrome oxidase activity than those grown at lower levels (Mondy et al., 1967). Although potassium in the soil did not affect PPO activity, the phenolic content and the discoloration of the harvested potatoes were affected by the potassium fertilizer. Temperature and organic content of the soil also seem to affect the chlorogenic acid content of Russet Burbank potatoes (Kaldy and Lynch, 1983).

Plant Molecular Biology. Bruising and other stress conditions induced PPO biosynthesis in potato plants (Belknap et al., 1990; Dyer et al., 1989). Related studies by Thipyapong et al. (1995) show that only potato tissues which are developmentally competent to express PPO mRNA respond to wounding by increased accumulation of PPO mRNA. Studies by Thygesen et al. (1995) revealed that five distinct cDNA clones encode a multigene PPO family in potatoes. A possible approach to reducing PPO activity and the consequent enzymatic browning reactions in potatoes is to characterize and inactivate the genes coding for PPO. Such inactivation was achieved by generating antisense RNA specific for target enzymes (Bachem et al., 1994; Hunt et al., 1993). The possible significance of this approach for browning prevention is discussed below under Research Needs.

Host-Plant Resistance. Lyon (1989) makes the following points about the contribution of phenolic compounds to phytopathogen resistance: (a) Phenolic compounds and derivatives are an important part of the general defense mechanism, especially against soft rot bacteria. They may function by inhibiting bacterial growth, by inhibiting cell wall-degrading enzymes, and/or as precursors in the formation of physical barriers. (b) Various phenolic compounds exhibit different specificities against *Erwinia* spp. (c) Phenolic compounds inhibit enzymes involved in pathogenesis, such as polygalacturonase from *Rhizobia solani* and glucan synthase from *Beta vulgaris.* (d) Polyphenols react with proteins to form insoluble tannins. The precipitated tannins inhibit pectinase in the cell walls by cross-linking reactions. (e) Both phenolics and phytoalexins appear to be involved in the resistance of potatoes to *Erwinia* spp.

Other studies confirmed that polyphenolic compounds impart resistance to potato tubers against soft rot caused by *Erwinia carotovora,* a major cause of losses of stored potatoes (Kumar et al., 1991). This effect is presumably due to the antibacterial activity of the phenolics or quinones formed by the action of PPO on phenolics. Although potato cultivars were more susceptible than somatic hybrids to *E. carotovora*-induced soft rot, no relation was observed between soft rot resistance and activity of polyphenol oxidase or peroxidase in intact, injured, or inoculated tissues (Loikowska and Holubowska, 1992). It is noteworthy that caffeic, chlorogenic, and ferulic acids were more effective against *E. carotovora* when used as mixtures in the proportions found in the periderm of potatoes than when used individually (Ghanekar et al., 1984). The chlorogenic acid in wounded periderm was generally higher in infected tubers than in the uninfected ones.

A major unknown is the contribution to plant resistance of each of the native phenolics, such as chlorogenic acid and tyrosine and their oxidation and condensation products including semiquinones, quinones, melanins, and suberins.

A histochemical test based on the reaction of chlorogenic with nitrous acid demonstrated an association of the polyphenol with physiological internal necrosis of potato tubers (Dinkle, 1964). Polyphenols, including flavonols, cinnamic acid derivatives, and coumarins, accumulate in the sound tissue adjacent to injured tissue in many types of vegetables and fruits. Compounds accumulating in Irish potato tissues as a result of wounding, exposure to pathogens, and virus infection include chlorogenic acid, scopoletin, scopolin, aesculetin, and caffeic acid. This accumulation of polyphenols in sound tissue adjacent to injured tissue seems to give host-plant resistance toward the pathogen. This resistance could result from the increased rate of metabolism induced by the injury and/or alteration of the normal metabolic pathways by the injury, leading to the accumulation of unused polyphenols normally metabolized (oxidized) by plant enzymes.

The formation of such wound-barrier layers occurs in sweet potatoes, Irish potatoes, carrots, beets, parsnips, squash, and turnips (Craft and Audia, 1962). The UV spectra of extracts of wounded sweet potatoes, Irish potatoes, and carrots exhibited enhanced maxima at 325 nm, associated with chlorogenic acid from suberized tissues. The peak decreased in intensity following oxidation.

These observations raise the possiblity of synergism between structurally related phenolic compounds in imparting resistance to bacteria. Such synergistic action could guide plant breeders to produce improved

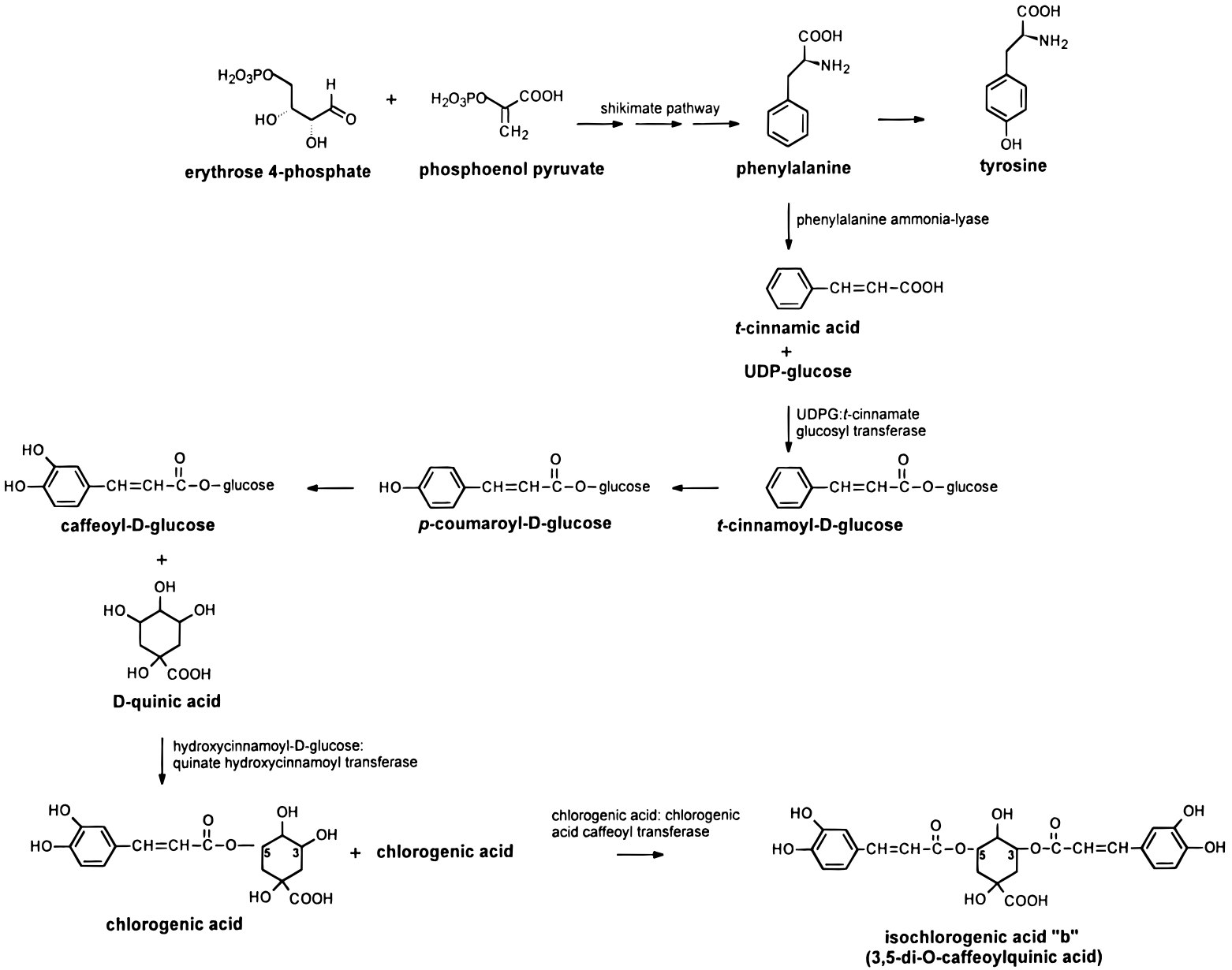

Figure 6. Biosynthetic pathways toward chlorogenic acid (Herrmann, 1995; Moriguchi et al., 1988; Schmidt and Amrhein, 1995; Tanaka and Kojima, 1991; Villegas and Kojima, 1986).

potato cultivars with the right mixture of structurally different phenolic compounds.

Glandular trichome-bearing leaves of wild potato cultivars such as *Solanum berthaulti* Hawkes are of interest to plant breeders because they confer resistance to several major foliage-feeding insect pests (Ave et al., 1986). Type A glandular trichomes confer insect resistance to the wild potatoes by oxidatively polymerizing their contents following breakage, leading to insect entrapment (Kowalski et al., 1993). Because *Solanum tuberosum* trichomes contain low amounts of PPO, they do not significantly contribute to host-plant resistance. The authors suggest that an ELISA for PPO in the glandular trichomes may assist in rapid introgression of the trichome-resistant trait of the wild potatoes into commercial *S. tuberosum* cultivars.

Selection of aphid-resistant hybrids can be improved by an improved enzymic browning assay (EBA) based on release of the exudate from tetralobulate (type A) trichomes of three leaflets in a test tube (Ave et al., 1986). The reagents change from pink to violet measured at 470 mu. The intensity of the color is related to the PPO and phenolic substrates of the trichomes, which interact to form a viscous substance as a result of oxidative transformation to polymeric materials.

Polyphenol oxidation is also important in the resistance of potatoes against slugs, which cause considerable damage to main crop potatoes (Johnston and Pearce, 1994). When potato tissues are damaged, polyphenols are enzymatically oxidized to quinones, which then polymerize to dark pigments. The rate of dark pigment formation seems to impart resistance. As is the case for other pathogens, quinones and polyphenolic tannins may inhibit slug digestion of potato tissue by binding to digestive enzymes in the gut and/or binding to proteins lowering protein digestibility. (See section below on Protein Nutritional Quality.) However, it is also possible that the slugs have an aversion to the oxidized polyphenols based on sensory perception.

Although differences in glycoalkaloid and sugar content could be related to susceptibility (to attack) of potatoes to wireworm, *Agrioles obscurus*, this was not the case for chlorogenic acid (Jonasson and Olsson, 1994; Olsson, 1989). Total glycoalkaloid content was the key factor in predicting larval feeding, accounting for 65% of the total variation. Differences in sugar levels of the diet (fructose plus glucose) accounted for 13%. Differences in chlorogenic acid or sucrose levels did not significantly affect the survival of the larvae.

No correlation was observed between chlorogenic acid content of different potato clones and their resistance to infection with potato leafroll virus (Lyon and Barker, 1984). Although levels of chlorogenic acid increased following infection of potato tubers with the fungus *Phytophthora infestans*, no differences in the levels were observed in resistant and nonresistant cultivars (Phukan and Baruah, 1991).

The cited studies suggest that although polyphenols may be involved in host-plant resistance, their involvement is selective; that is, they protect only against some but not all potato phytopathogens. A need exists to better define their contribution to the overall protection in which other resistance compounds also participate. This is a challenging problem since the concentrations of the various compounds appears to be cultivar-dependent, so that specific combinations found in different varieties need to be tested to assess optimum combinations for possible synergism in phytopathogen resistance (Fewell and Roddick, 1993; Rayburn et al., 1995).

STORAGE AND PROCESSING

Effects of Storage. Ontario and Pontiac potatoes, cultivars susceptible and resistant to precooking blackening, respectively, had higher cytochrome and polyphenol oxidase activities when stored at 50 °F than at 40 °F (Mondy et al., 1966). Less PPO activity was observed at the lower temperature. This may explain the observed greater polyphenol content at the lower temperature, since enzyme activity would be expected to be indirectly related monomeric polyphenol content. That is, the greater the activity, the greater the transformation of monomeric polyphenols to polymeric ones. The higher PPO activity at the higher storage temperature may account for the greater discoloration due to transformation of polyphenols to polymeric pigments at that temperature. Leja (1989) found that the total phenolic and chlorogenic acid content was the same in stored mature potato tubers with undeveloped periderm as in mature tubers. Although high-temperature storage did not affect the total phenolic and chlorogenic acid content, both levels increased on prolonged (5 week) storage at 0 °C.

Freshly harvested as well as stored potatoes produced phenolic compounds and phytoalexins after infection with soft rot bacteria *E. carotovora* and dry rot fungi *Fusarium* spp. (Rober, 1989). Uninfected control potatoes synthesized only low levels of these compounds. Infection of potato tubers evidently induces a cascade of metabolic transformations during storage, leading to the production of secondary metabolites involved in host-plant resistance.

In addition to changes in polyphenol content, potato storage induces other compositional changes depending on conditions used. For example, Nakagawa et al. (1995) report the following findings for potato tubers stored at 4, 20, and 33 °C. Sprouting occurred after about 30 days at 20 °C but not at 4 or 33 °C after 160 days. Tubers transferred to 33 °C after 70 days at 20 °C did not sprout during the next 160 days. Respiration rates were initially high but decreased during storage. Reducing sugar content of tubers stored at 33 °C was lower than in tubers stored at 4 °C. PPO activity in tubers stored at 20 °C increased 2-fold during storage, but rapidly decreased at 33 °C.

Storage-related light- and γ-radiation-induced changes in polyphenol content of potatoes are described below.

Effects of Light. Potatoes contain polyphenolic compounds, glycoalkaloids, and proteins. Some of the proteins have the ability to inhibit trypsin, chymotrypsin, and carboxypeptidase (Brown et al., 1986; Dao and Friedman, 1994; Lisinska and Leszczynski, 1989; Weder, 1989). Light, mechanical injury, temperature extremes, and sprouting induce an increase in the glycoalkaloid content, which can range up to 5 times original levels. Exposure to light after harvest also leads to surface greening, which is accompanied by increases in chlorogenic acid and chlorophyll biosynthesis.

The increase in glycoalkaloid content may be undesirable since it could impart a bitter taste to potatoes (Kaaber, 1993; Johns and Keen, 1986; Mondy and Gosselin, 1988; Zitnak and Filadelfi-Keszi, 1988) and make them less safe (Friedman and McDonald, 1997; Friedman et al., 1996). Since chlorogenic acid, glycoalkaloids, and protease inhibitors may act as so-called antifeeding agents in potatoes, protecting potatoes from attack by phytopathogens and insects, the question arises whether suppression of biosynthesis of alkaloids, one of our current objectives (Moehs et al., 1996a,b,

1997; Stapleton et al., 1991, 1994), will result in compensatory changes in the biosynthesis of chlorogenic acid and/or protease inhibitors. Although the biosynthetic pathways leading to the formation of these resistance factors are probably unrelated, expectations are that in response to stress and reduced formation of one class of compounds, potato plants may increase the synthesis of the others.

To develop a better understanding of the dynamics of secondary metabolite formation, potatoes were stored in the dark and under fluorescent light for various time periods and analyzed for chlorophyll, chlorogenic acid, α-chaconine, α-solanine, and inhibitors of the digestive enzymes trypsin, chymotrypsin, and carboxypeptidase A (Dao and Friedman, 1994). Specifically, exposure of commercial White Rose potatoes to fluorescent light for 20 days induced a time-dependent greening of potato surfaces and an increase in chlorophyll, chlorogenic acid, and glycoalkaloid content, but no changes in the content of inhibitors of the digestive enzymes trypsin, chymotrypsin, and carboxypeptidase A. Storing potatoes in the dark did not result in greening or chlorophyll formation. Chlorogenic acid and glycoalkaloid levels of dark-stored potatoes did increase, but less than in the light-stored potatoes. In the light, chlorogenic acid concentration increased from 7.1 mg/100 g of fresh potato weight to a maximum of 15.8 mg after greening. An approximate 300% light-induced increase for each glycoalkaloid was also observed. Experiments on delay of greening by immersion in water suggest that the concentration of chlorophyll is 26 times greater, that of chlorogenic acid and glycoalkaloids 7−8 times greater, and that of protease inhibitors about 2−3 times lower in the peel of the green potatoes than in the whole tuber after storage.

Griffiths et al. (1995) also reported that exposure of potatoes to light induces significant increases in chlorogenic acid content. This increase appears to be cultivar-dependent since the magnitude of the increase correlated with the initial value found in unexposed potatoes. The light-induced increase in chlorogenic acid may result from light induction of phenylalanine deaminase, which catalyzes the biosynthesis of chlorogenic acid (Zucker, 1965).

In related studies, Laanest et al. (1995) observed a rapid increase in the content of chlorogenic acid and other phenolic compounds in light-exposed sliced potatoes stored for 9 days. Formation of polyphenols in the tubers was accompanied by the appearance of flavonoids. The authors suggest that activity of the shikimate pathways during healing of potato tubers after exposure to light is not rate-limiting to the biosynthesis of phenols.

Effects of γ-Radiation. γ-Radiation effectively prevents sprouting and protects potatoes during storage against damage by fungi and other phytopathogens (Swallow, 1989). This is a desirable objective since when potatoes sprout, they decrease in weight, quality, and market value. Sprouts may also present a health hazard, being high in glycoalkaloids. Different investigators report different results on the effect of γ-radiation on chlorogenic acid and related phenolic content of potatoes. Some of the relevant studies are summarized below.

Penner and Fromm (1972) used a quantitative TLC method for the direct determination of chlorogenic acid in irradiated potatoes. Chlorogenic acid content rose immediately after irradiation and then returned to normal values within several weeks of storage.

Bergers (1981) found a time-dependent decrease in chlorogenic acid and a glycoside of scopoletin after potato tubers were irradiated up to 3 kGy. Irradiation had no effect on the glycoalkaloid content of the potatoes. A dose as low as 0.1 kGy was sufficient to inhibit sprouting with minimal compositional changes in the treated potatoes. Infection by fungi also led to an accumulation of scopolin (Clarke, 1976). Mondy and Gosselin (1989) found that irradiation increased discoloration and phenolic content and decreased lipid and phospholipid content of potatoes. Irradiated potatoes stored at 5 °C had a higher total phenol content than those stored at 20 °C. These authors also report that a radiation dose of 10 krad caused less darkening than a higher dose. The increased blackspot formation at higher doses may have been due to rupture of lipid membranes. This rupture may liberate PPO from mitochondria, allowing it to contact phenolic substrates in the vacuole, causing enzymatic darkening. Darkening could therefore be minimized by controlling the dose.

Irradation of tubers to inhibit sprouting caused reduction in both total phenolic and chlorogenic acid contents. Increased formation of potato phenolics was observed during storage of tubers following irradiation (Ramarmurthy et al., 1992; Table 7). The HPLC analysis revealed that three chlorogenic acid isomers accounted for about 88% of the total phenolics measured by HPLC. The formation and accumulation of *neo* and *crypto* isomers of chlorogenic acid during storage after exposure to radiation are also noteworthy.

γ-Irradiation up to 10 krad had no effect on the defense mechanism at the site of injury of potatoes, i.e., the formation of quinones from phenolic acids (Pendharkar and Nair, 1987). Irradation of tubers to inhibit sprouting caused reduction in both total phenolic and chlorogenic acid contents. Specifically, it reduced by about 50% the ability of tubers to synthesize chlorogenic and caffeic acids in the irradiated tissue. The radiation also impaired the induction of cinnamic acid-4-hydroxylase but not phenylalanine ammonia lyase, both of

Table 6. Millimolar Concentration of Inhibitors Required To Reduce 400 Units of PPO/mL by 50% (I_{50}) at 25 °C and PPO in Potato Suspensions (Friedman and Bautista, 1995)[a]

inhibitor	I_{50} (pure PPO)	I_{50} (potato suspensions)
L-cysteinylglycine	0.43	1.85
L-cysteine	0.35	1.09
N-acetyl-L-cysteine	0.27	1.16
homocysteine	0.23	1.17
sodium bisulfite	0.21	0.54
L-cysteine ethyl ester	0.12	1.60
reduced glutathione	0.12	2.18
L-cysteine methyl ester	0.12	1.60

[a] The lower the value, the more potent the inhibitor.

Table 7. Changes in Phenolic Compounds (Milligrams per 100 g Fresh Weight) in Potatoes during Storage following Irradiation [Adapted from Ramarmurthy et al. (1992)]

	storage period (days)					
phenenolic compound	0	4	6	8	10	15
3-*O*-caffeoylquinic acid (*neo*-chlorogenic acid)		13.6	24.2	24.2	31.4	11.7
4-*O*-caffeoylquinic acid (*crypto*-chlorogenic acid)		5.8	10.4	10.4	13.4	3.9
5-*O*-caffeoylquinic acid (chlorogenic acid)	4.5	34.1	60.8	78.8	38.2	28.5
caffeic acid	1.8	5.7	6.4	7.8	6.8	4.9
p-coumaric acid	1.6	4.5	5.0	5.1	4.4	3.5
ferulic acid	1.3	3.1	4.0	4.4	4.0	3.2
total	9.3	66.7	110.8	140.9	75.8	56.7

Table 8. Oxidation Potentials (in Volts) of Selected Phenolic Acids at pH 4.7 [Adapted from Felice et al. (1976)]

phenolic acid	potential
3,4-dihydoxycinnamic (caffeic)	0.35
chlorogenic	0.39
3,4-dihydroxyphenylpropionic (dihydrocaffeic)	0.43
3,4,5-trihydroxybenzoic (gallic)	0.46
3,4-dihydroxybenzoic (protocatechuic)	0.52
4-hydroxy-3,5-dimethoxybenzoic (syringic)	0.55
4-hydroxy-3-methoxycinnamic (ferulic)	0.57
4-hydroxy-3-methoxybenzoic (vanillic)	0.72
4-hydroxycinnamic (*p*-courmaric)	0.73
4-hydroxyphenylacetic	0.77
4-hydroxybenzoic	0.99

which are involved in chlorogenic acid biosynthesis. A related study on the phenylpropanoid metabolism in γ-irradiated and unirradiated potato tubers revealed a depletion of chlorogenic acid following irradiation during the 21-day postirradiation storage period (Penharkar and Nair, 1995). The loss in chlorogenic acid was associated with both its impaired synthesis and its accelerated conversion to ferulic and sinapic acids. The latter were deposited in the lignin part of the tuber.

Generally, γ-radiation can suppress wound periderm formation, thus favoring pathogen access to wounds. A defense mechanism against this effect is the formation of quinones via oxidation of phenolic compounds by PPO released by rupture of the potato tissue. The quinones then polymerize to defensive polymers at the site of the tissue injury, as discussed earlier.

Thomas and Delincee (1979) found that γ-radiation at sprout-inhibiting doses did not prevent suberization of potato tissues. Postirradiation healing of tissues was accompanied by the deposition of suberin, a polymer derived from polyphenols and fatty acids. Such suberization prevents weight loss and permanent damage to potatoes.

An increase in polyphenol oxidase activity was noted after potatoes were irradiated at 2 krad (Cheung and Henderson, 1972). In contrast, the activity of the enzyme decreased when the radiation dose was increased. Prolonged postirradiation storage of the potatoes also resulted in lower enzyme activity.

Considerable browning occurs in stored potatoes which are then exposed to γ-radiation, especially in the cortex and along the xylem (Ogawa and Uritani, 1979). Observed browning was accompanied by a marked increase in polyphenol content and peroxidase activity and a transient decrease in PPO activity. The extent of browning strongly depended on the storage period from harvest to irradiation. These authors recommend that, to minimize browning, potatoes should be stored at ambient temperature for about 1 month before irradiation.

Peeling of potatoes prior to boiling reduces the intensity of γ-radiation-induced after-cooking darkening of the tuber flesh (Thomas, 1981). Presumably, leaching of polyphenols from the flesh into the cooking water minimizes the availability of polyphenols to form dark iron complexes. The amount of leaching into the cooking water was 3−5 times greater in prepeeled tubers than in whole tubers. It is also possible that leaching of ferrous compounds into the cooking water also contributes to reduced darkening.

Leszczynski et al. (1992) found that (a) γ-radiation inhibited sprouting of potatoes, (b) the irradiated tubers had lower starch and higher sucrose contents, (c) radiation produced darker potatoes, and (d) radiation had no or minimal effects on the quality of potato chips made from the treated potatoes. Since radiation inhibited sprouting during storage, the production of good quality chips was easier from irradiated than from control potatoes.

The described studies report apparently contradictory results about elevation or decreases in polyphenol content of potatoes following irradiation. Possible explanations for these results include (a) differences in radiation doses and exposure times used by different investigators, (b) storage history of the potatoes before exposure to radiation, and (c) differences in genotype susceptibilities to effects of radiation. These varietal-related differences could be governed by differences in enzyme profiles involved in biosynthesis of polyphenols, differences in moisture content and/or porosities (Lulai and Orr, 1995) of the potato tuber surfaces that may affect peneteration of radiation, or some as yet undefined parameters. For each cultivar, a need exists to define minimum radiation conditions to prevent sprouting and to destroy phytopathogens while minimizing undesirable compositional changes.

DIETARY SIGNIFICANCE

Bruising-Induced Potato Discolorations. Potatoes may undergo browning and other discolorations (depicted in Del Zan and Baruzzini (1991) with color photographs of whole and sliced potatoes) both during growth and after harvest. Internal blackspot in potatoes is caused by internal enzymatic browning type reactions initiated by PPO catalysis with tyrosine as the primary substrate. According to Shetty et al. (1991), bruising of potatoes induces these undesirable pigmentations as well as shrinkage, rotting, and major economic losses. This subsurface physiological discoloration resulting from mechanical injury is a leading cause of rejection of shipments in potato production. In addition to blackspot formation, bruising induces the postharvest biosynthesis of glycoalkaloids, which could adversely impact safety (Friedman, 1992; Friedman and McDonald, 1997).

Mapson et al. (1963) found a correlation between tyrosine, the activity of PPO, and the rate of browning in different potato varieties. No such correlation was found for chlorogenic acid and browning. Pavek and colleagues extensively studied the relationship of tyrosine to internal blackspot resistance and the inheritance of blackspot bruise resistance in potato (Corsini et al., 1992; Pavek et al., 1985, 1993; Stark et al., 1985). Enzymatic discoloration was highly correlated with total phenolic ($r = 0.89$) and free tyrosine levels ($r = 0.85$) in potatoes. Dean et al. (1992, 1993) describe three techniques for measuring blackspot pigment development in progeny of potato crosses with various degrees of resistance to blackspot formation. The transfer of resistance of bruise-resistant genotypes to progeny in crosses with susceptible genotypes correlated with tyrosine content. The relative rate of tyrosine synthesis in a blackspot-resistant potato cultivar was about 55% less than in the susceptible cultivar Lemhi Russet. On the other hand, Mondy and Munshi (1993) report that although free tyrosine was positively correlated with discoloration within a cultivar, it did not appear to be the predominant factor determining blackspot susceptibility of potatoes, since the blackspot-susceptible cultivar, Ontario, had higher ascorbic acid and lower tyrosine contents than the resistant cultivar, Pontiac. Moreover, ascorbic acid and enzymatic discoloration were not consistently correlated with each other in spite of the fact that the vitamin appears to function as an

antioxidant in the process of discoloration. The lipid content of Chippewa and Katahdin potatoes, although low, is also important in cellular integrity and resistance to bruising (Mondy and Mueller, 1977). Evidently, tyrosine-initiated blackspot formation varies in different potato cultivars and may be modulated by ascorbic acid and lipids. Lemhi Russet potatoes are available with enhanced resistance to bruising-induced blackspot formation (Love et al., 1993).

The described results show that a variety of environmental factors influence storage-induced compositional changes in potatoes. The observed changes should help define consequences of potato breeding, blackening, and greening for plant physiology, food quality, and food safety. Specifically, this information should be useful for breeding potato varieties with an initial low chlorogenic acid content to minimize both content and rate of increase, e.g., to minimize after-cooking darkening and/or enzymatic browning during food processing, if that is the objective. However, since chlorogenic acid is reported to exert beneficial effects on health as described below, another desirable objective might be to breed for high-chlorogenic acid varieties and/or enhance the chlorogenic acid content by post-harvest exposure to light and other stress conditions. Possible implications of these changes for handling and marketing of potatoes are also discussed below under Research Needs.

After-Cooking Darkening. Chlorogenic acid seems to be responsible for bluish-gray discoloration of boiled or steamed potatoes following exposure to air. This so-called "after-cooking blackening or darkening", which can occur within a few minutes after steam peeling, is perceived by some consumers as undesirable. Chemically, the blackening appears to be due to the formation of a colorless reduced ferrous ion−chlorogenic acid complex in the potato. The ferrous complex is then oxidized to a dark ferric complex following exposure to oxygen in the air. Such darkening of potatoes has been extensively studied (Heisler et al., 1969; Hughes and Swain, 1962; Muneta and Kaisaki, 1985; Putz, 1995). The potential for darkening can be measured in two ways: (a) by a test involving a waiting period of 1−12 h for full color development after steaming; and (b) by a chemical test based on reaction of chlorogenic acid with a mixture of urea, tartaric acid, and sodium nitrite (Mann and Lambert, 1989). The latter is a rapid, histological staining method based on the formation of a cherry-red color of nitrosylated chlorogenic acid. The histological method for visualizing chlorogenic acid in potato tissues agreed with after-cooking darkening in a blanching fry test.

Blackening tendency appears to be directly related to the size of the potato tubers (Siciliano et al., 1969). This trend presumably results from the fact that the stems of large tubers have low citric acid content, high potassium−citric acid ratios, and low citric acid−polyphenolic ratios compared to smaller ones. Citric acid and other chelating agents inhibit potato blackening by competing with chlorogenic acid for ferrous ion chelating sites. The after-cooking darkening of Spartan Pearl potatoes was correlated with phenolic but not citric acid content (Silva et al., 1992).

Mann (1995) described a process for minimizing after-cooking darkening in French fried potatoes: treatment of water-blanched, fried potato strips, which often discolor on exposure to air, with a combination of calcium acetate and an oxidation inhibitor. The preventive effect is presumably due to both the inhibitor and the complexation of the calcium ions with chlorogenic acid on the surface of the potato strips, preventing formation and oxidation of the chlorogenic acid−ferrous ion complex that causes darkening.

Ascorbic acid plus ferrous iron forms a purple pigment similar to the chlorogenic acid−iron complex (Muneta and Kaisaki, 1985). The ascorbate complex is less stable, however. Strong chelating agents, including citric acid, EDTA, and sodium hydrogen pyrophosphate, suppressed color formation resulting from both complexes.

Muneta and Kalbfleish (1987) describe a heat-induced contact discoloration in boiled potatoes, an irregular brown ring near the edge of the contact zone where the unpeeled potato touches the bottom of the pan. Peeling potatoes or keeping unpeeled potatoes away from the bottom of the pan prevents dark ring formation. The heat-induced contact discoloration may result from enzymatic-type browning reactions similar to those that may be responsible for blackspot and prepeeling blackening of potatoes. Specifically, rings can occur at some point along a decreasing temperature gradient where the dominant effect is tyrosinase activation by heat (leading to browning), rather than heat inactivation of the enzyme. At some still lower temperature, heat inactivation of the enzyme or leakage of substrates from heat-damaged cell membranes no longer occurs, stopping heat ring formation.

Although blackspot formation in potatoes may arise from nucleophilic addition reactions of amino groups to oxidized polyphenols described below (Stevens and Davelaar, 1996), nonenzymatic browning reactions of free amino acids and proteins with reducing sugars such as glucose could also explain the heat-induced and related discolorations. Such reactions are described in detail elsewhere (Felton et al., 1992; Friedman, 1994, 1996a,b).

The green color of potato cooking waters appears to be due to a pigment derived from the reaction of chlorogenic acid and glutamine (Adams, 1994). Whether the heat-induced discolorations adversely affect the nutritional value of the boiled and darkened potatoes is not known.

Browning Prevention. The sulfhydryl (SH or thiol) compounds such as cysteine, *N*-acetyl-L-cysteine, and reduced glutathione, as well as ascorbic and citric acids, are good inhibitors of the enzyme PPO which catalyzes enzymatic browning in fruits and vegetables including potatoes (Dudley and Hotchkiss, 1989; Friedman et al., 1991; Golan-Goldhirsh et al., 1994; Langdon, 1987; Matheis, 1987a,b; Matheis and Whitaker, 1984; Muneta, 1981; Muneta and Walradt, 1968; Sanchez-Ferrer et al., 1993; Sapers, 1993; Sapers and Miller, 1992, 1995). We showed that SH-containing amino acids and peptides are good inhibitors of both enzymatic and nonenzymatic browning in freshly prepared and commercial fruit juices, apples, fresh and dehydrated potatoes, heated amino acid−carbohydrate mixtures, and protein-rich foods (Friedman and Bautista, 1995; Friedman and Molnar-Perl, 1990; Friedman et al., 1992; Molnar-Perl and Friedman, 1990a,b; Figure 7).

In some applications, the effectiveness of some of these compounds on a molar basis approached that of sodium sulfite, the use of which is being discontinued because many asthmatic individuals are sensitive to it (FDA, 1990). However, in searching for the most potent and safe replacement for sodium sulfite, it became apparent that the potency of different thiols as PPO inhibitors varies widely, depending on both the structure of the thiol and the environment in which the inhibition is carried out. To compare relative effectiveness of structurally different thiols in a food matrix as

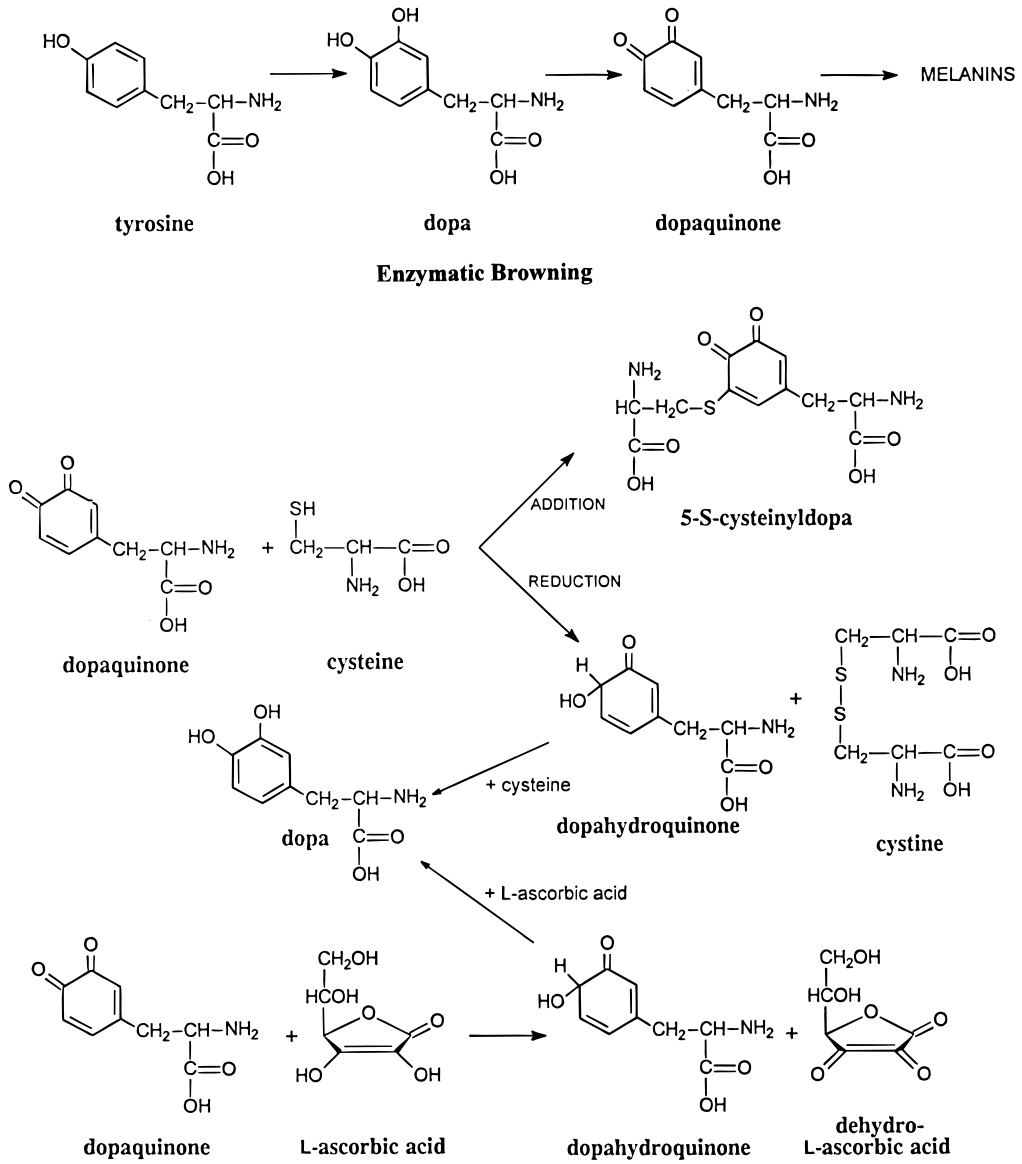

Figure 7. Transformation of tyrosine to melanin via DOPA and dopaquinone (enzymatic browning) and postulated inhibition of enzymatic browning by cysteine and ascorbic acid by trapping the dopaquinone intermediate.

well as in pure enzyme solution, we evaluated the effectiveness of a series of sulfhydryl compounds in PPO solutions and in dehydrated potato suspensions at 25 °C. These inhibitors were less effective in the potato suspensions, and the relative effectiveness of structurally different thiols differed from those observed in PPO solutions. Table 6 shows relative inhibitory potencies of several thiols against pure PPO and in the suspensions.

Although the reasons for these differences are not apparent, possibilities include slow diffusion of the inhibitors to PPO and substrates in the heterogeneous dehydrated potato suspension, the action of PPO on substrates other than tyrosine such as chlorogenic acid (Friedman and Smith, 1994), and the reaction of the thiols with carbohydrates. The latter reactions may also be beneficial since they may prevent nonenzymatic browning.

These considerations suggest that no general conclusions can be made about the PPO inhibition by thiols in specific foods. Each food category has to be evaluated separately with each sulfhydryl compound to find optimum conditions to prevent both enzymatic and nonenzymatic browning under specific conditions of storage, transport, and processing.

Our studies show that SH-containing compounds, especially cysteine ethyl ester and reduced glutathione, are potent inhibitors of PPO. They are therefore potential sulfite substitutes for browning prevention. Since the effectiveness of a specific sulfhydryl compound is influenced by its structure, additional studies are needed to optimize the antibrowning action of a variety of structurally different SH-containing amino acids and peptides with different physicochemical properties.

Since safety considerations will determine regulatory approval and commercial use of SH-containing amino acids and peptides as browning inhibitors, it should be noted that L-cysteine is on the GRAS (generally accepted as safe) list and is widely used as an antioxidant in baking formulations (Friedman, 1996b). Reduced glutathione is a naturally occurring tripeptide present in many foods (Jones, 1992). Although *N*-acetyl-L-cysteine does not occur naturally, it is used as a drug ("Mucomyst") to reduce lung congestion (Friedman, 1973). The compound is an excellent nutritional source of cysteine for humans and animals (De Bernardi di

Valserra et al., 1989; Friedman and Gumbmann, 1984), and acts as an antimutagen and anticarcinogen (De Flora et al., 1989; Friedman et al., 1982a; Stevens et al., 1995).

Efforts are continuing to develop sulfite substitutes for browning prevention in potatoes and other foods. For example, Sapers and Miller (1995) inhibited potato discoloration for 14 days at 4 °C by using a double treatment, ascorbic/citric acid solutions plus heat, followed by dipping in a solution containing ascorbic and citric acids plus sodium acid pyrophosphate. Almeida and Mogueira (1995) evaluated the effectivness of combinations of several inhibitors and heat in reducing PPO activity in fruits and vegetables. Ascorbic plus citric acid and heat proved the best combination. The apparent formation of inclusion complexes of chlorogenic acid with β-cyclodextrins could also provide a basis for controlling enzymatic browning in potatoes (Irwin et al., 1996).

Flavor and Taste. Sinden et al. (1976) found a correlation between glycoalkaloid content and undesirable potato flavor, but no significant correlation between phenolic content and either bitterness or burning sensation. In contrast, Mondy et al. (1971) report a positive correlation between phenolic content and bitterness and astringency of potatoes.

Since potatoes contain both glycoalkaloids and polyphenols in various amounts depending on variety, the net effect on taste and flavor could be the result of combined, possibly additive, synergistic, or antagonistic effects of both components (Johns and Keen, 1986; Kaaber, 1993; Zitnak and Filadelfi, 1985).

Antioxidative Activities. Polyphenolic compounds in potatoes show antioxidative activity in several food systems. For example, Onyeneho and Hettiaachchy (1993) evaluated the abilities of freeze-dried extracts from the peels of six potato varieties to prevent soybean oil oxidation. Using an active oxygen method, they found that 20 g of soybean oil treated with 50 mg of the extracts had a lower peroxide value (PV, 22−28) than did a control oil sample (PV, 109). HPLC and TLC studies suggested that chlorogenic and protocatechuic acids were the main antioxidants in the extracts. Peels from red potatoes contained greater amounts of polyphenols than those from brown-skinned varieties.

In related studies, Rodriguez de Sotillo et al. (1994a,b) confirm the strong antioxidant activity of freeze-dried extracts of potato peel waste in sunflower oil. The total polyphenolic content of the peel determined by HPLC consisted of 50.3% chlorogenic acid, 41.7% gallic acid, 7.8% protocatechuic acid, and 0.21% caffeic acid. Al-Saikhan et al. (1995) found that the phenolic content and antioxidative activity of four potato cultivars was genotype-dependent and not related to flesh color. These results suggest the possible value of potato peel in the prevention of oxidative rancidity of food oils.

As part of an effort to develop an HPLC method for plant phenolics with amperometric detection, Felice et al. (1976) measured the anodic oxidation potentials of structurally different compounds. The low values for caffeic and chlorogenic acids (Table 7) suggest that the presence of the acrylic acid group in these compounds conjugated with the aromatic ring facilitates oxidation to the corresponding quinones. The free electron of peroxy radicals present in oxidized fatty acids or lipoproteins can be abstracted. Generally, phenols are more reactive with the peroxy radicals than the corresponding quinones. On the other hand, quinones are better metal-chelating antioxidative agents. Both aspects operate in the antioxidative effect. The free electron on

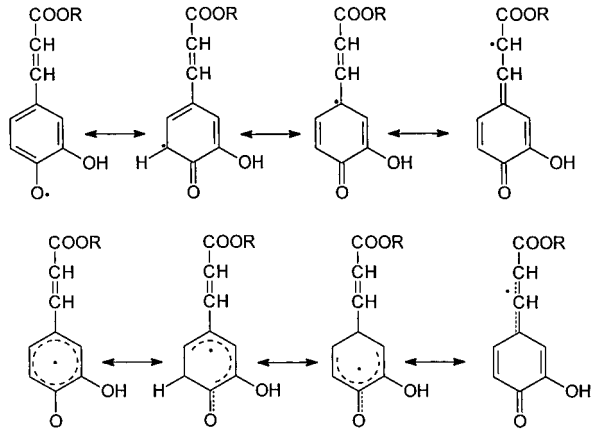

Figure 8. Resonance stabilization of a phenoxyl radical through delocalization of the free electron throughout the conjugated system of chlorogenic acid: (top) resonance forms in which the free electron is localized on oxygen or carbon; (bottom) delocalized electron. The actual resonance structure is a hybrid of the depicted forms (Wheland, 1955). The depicted quinone radical is more stable (has a lower ground-state energy) than, for example, a linoleic acid peroxy radical. Mixing chlorogenic acid with such a peroxide would therefore result in transfer of the electron from the peroxide to the electron sink of chlorogenic acid (antioxidative effect).

the resulting quinone radical is then stabilized by dissipation of the charge through the conjugated system (Figure 8). The latter radical is therefore much less reactive than the peroxy radical (Halliwell et al., 1995; Larson, 1988; Newmark, 1984, 1987). Thus, the oxidation potentials of polyphenols in various food environments may be useful for predicting their relative potencies as antioxidants. In related studies, Foti et al. (1996) describe structure−antioxidative activities of phenolic compounds in micelles.

Elsewhere, we examined in detail the kinetics, mechanisms, and synthetic aspects of related nucleophilic addition reactions of protein functional groups to conjugated double bonds (Cavins and Friedman, 1967, 1968; Friedman, 1966, 1973; Friedman and Romersberger, 1966; Friedman et al., 1982b). The oxidation of a polyphenol to a quinone followed by participation of the quinone in such nucleophilic addition reactions is also mechanistically analogous to the corresponding oxidation of a porphyrin to a dehydroporphyrin intermediate followed by the addition of nucleophiles to the dehydroporphyrin. These studies should facilitate the design of experiments for the synthesis of chlorogenic acid and related quinone adducts for biological evaluation.

Antimutagenic and Anticarcinogenic Effects. Generally, inhibition of mutagenicity and of cancer development by polyphenolic compouds could be due to their ability to scavenge and trap potentially DNA-damaging electrophiles, free radicals, and toxic metals, to inhibit enzymes that activate precarcinogens to carcinogens, and to induce carcinogen-detoxifying enzymes (Friedman and Smith, 1984; Tanaka, 1994; Tanaka et al., 1993). The mechanisms of these possibilities need to be further elucidated.

Reported antigenotoxic and anticarcinogenic effects of both free and potato-bound chlorogenic acid include the following: (a) Nitrites in food can react with secondary amines to form mutagenic and carcinogenic nitrosamines. Chlorogenic acid and other polyphenols are reported to block nitrosamine formation by competitively reacting with the nitrite (Kikugawa et al., 1983). (b) Chlorogenic acid and several other simple phenolic acids also inactivate the mutagenicity of afla-

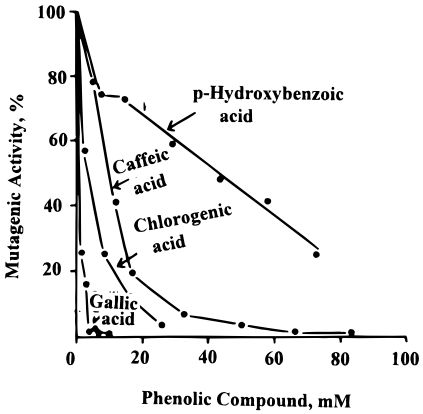

Figure 9. Inactivation of of mutagenic activity of aflatoxin B_1 by phenolic compounds [adapted from Stich and Rosin (1984)].

toxin B_1 (Figure 9). (c) A model system containing cellulose plus chlorogenic acid bound 100% of the carcinogen benzo[*a*]pyrene compared to 66% by cellulose alone and 32% by a cellulose−quercetin mixture (Camire et al., 1995). (d) Potato peel bound more of the benzo[*a*]pyrene than did wheat bran, cellulose, or arabinogalactan. Extrusion of the peel at 110 °C reduced the affinity of the carcinogen for the potato peel. Such extrusion may result in the destruction of chlorogenic acid. Camire et al. (1995) speculate that chlorogenic acid in the peel may interact with benzopyrene to form an insoluble complex, possibly as does chlorophyll with carcinogenic heterocyclic amines (Friedman, 1996b). (e) The protective effect of caffeic acid esters against DNA damage induced by hydrogen peroxide seems to be due to the *o*-dihydroxy structure of the esters (Nakayama et al., 1996).

It should also be pointed out that peel polyphenols may have little dietary significance if the polyphenols are destroyed during processing (baking, cooking, frying) and unless they are also present in the peeled potatoes (flesh). As mentioned earlier, destruction of chlorogenic acid appears to be least during microwaving. Note that the peel of baked or fried potatoes is the principal source of peel in the human diet (Bushway et al., 1984; Friedman and Dao, 1992). It may therefore be desirable to develop new, health-promoting potato peel-rich food formulations.

Glucose-Lowering Properties. Thompson et al. (1983) report that the polyphenol content of potatoes,

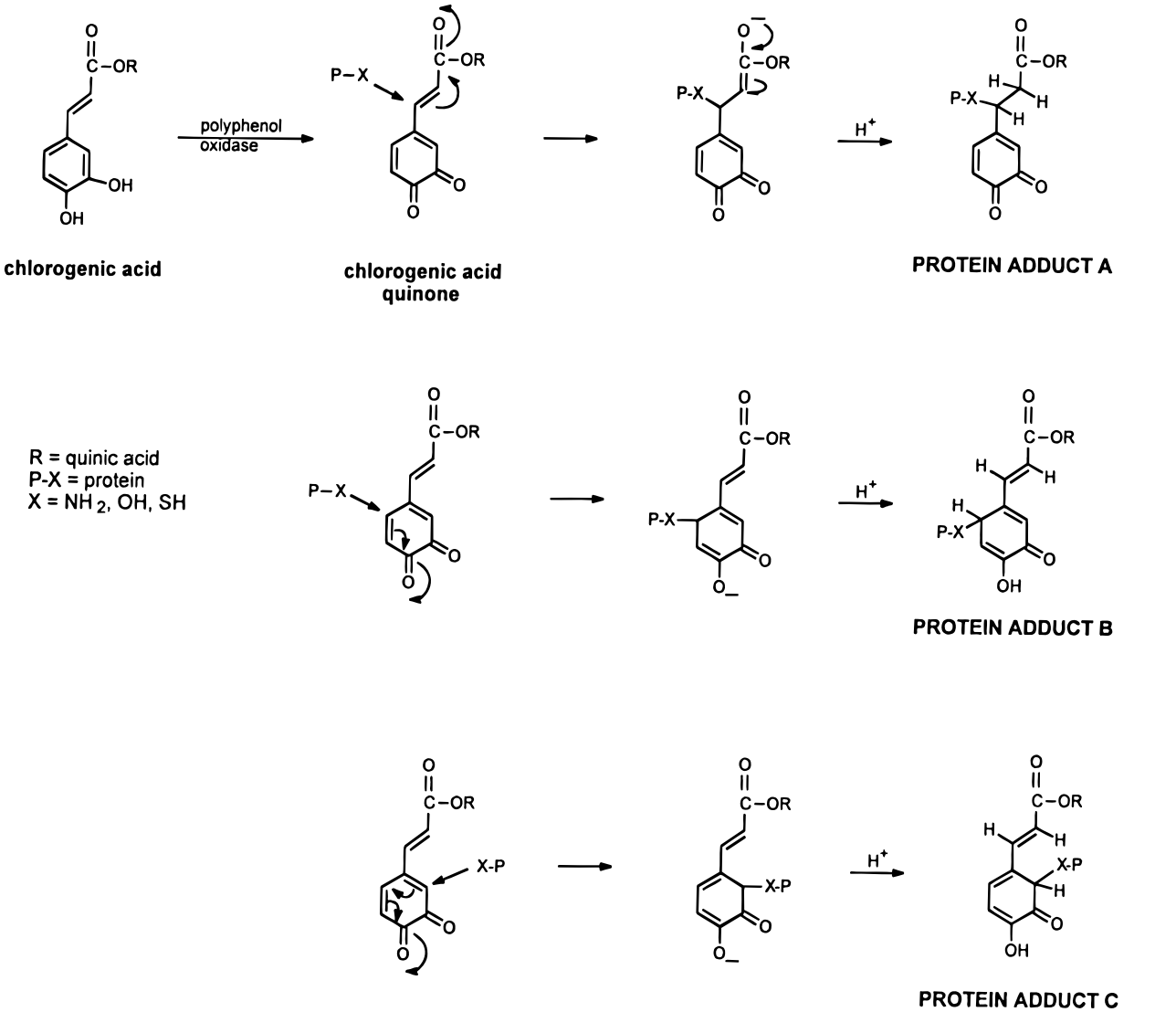

Figure 10. Nucleophilic addition reactions of protein functional groups to the conjugated systems of chlorogenic acid quinone. Addition can take place at the acrylate ester side chain to form product A and at two positions of the quinone ring to produce the derivatives B and C. In addition, each of the trigonal carbon atoms with which P−X combines becomes tetrahedral and asymmetric, creating the possibility of two diastereoisomers in each case. Losses of chlorogenic acid during baking shown in Figure 5 may be due to these and related transformations during food processing.

legumes, and cereals correlated negatively with the blood glucose response (glycemic index) of normal and diabetic humans consuming them in a controlled study. The glucose-lowering effect of the polyphenols may arise from their ability to inhibit amylases (which catalyze the hydrolysis of starch to glucose), phosphorylases (which are involved in starch metabolism), and proteolytic enzymes (that catalyze the hydrolysis of proteins to free amino acids in the digestive tract) and/or from their ability to direct complexation between the polyphenols and starch, preventing digestion. Another possibility is prevention of *in vivo* nonenzymatic browning between plasma glucose and amino groups of hemoglobin, which occurs under physiological conditions and which contributes to the cause of diabetes (Friedman, 1996b). Prevention of nonenzymatic browning by polyphenols could occur in two ways. First, antioxidative polyphenols could block oxidative steps in the multistep nonezymatic browning reactions. A less likely possibility is that polyphenol-derived quinones could competitively interact with amino groups, as shown in Figure 10, thus minimizing amino−carbohydrate reactions.

Cholesterol-Lowering Effects. Chlorogenic acid and other polyphenols also exhibit strong *in vitro* antioxidant activity for heart disease-related lipoproteins (Vinson et al., 1995). Since *in vivo* oxidation of lipoproteins (LDL) appears to be a major cause of heart disease, it is possible that chlorogenic acid and other polyphenols may also lessen heart disease.

In a relevant study, Lazarov and Werber (1996) found that consumption of potato peel induced a lowering of cholesterol in rats. They ascribe this result to the fiber content of the peel. However, it is likely that polyphenolic and other antioxidants as well as glycoalkaloids in the peel contribute to the observed hypochelesterolemia. Both tomato and potato glycoalkaloids have a strong affinity for cholesterol (Friedman et al., 1997; Roddick, 1979).

Protein Nutritional Quality. While behaving as antioxidants in foods and *in vivo,* semiquinones and quinones formed on oxidation of polyphenols can also simultaneously react with other molecules including amino acids and structural and functional proteins (Friedman, 1994; Hurrell and Finot, 1984; Matheis and Whitaker, 1984; Stevens and Davelaar, 1994). For example, Figure 10 shows some possible protein derivatives that can form from reaction of chlorogenic acid quinone with active-hydrogen-bearing protein functional groups such as ϵ-NH_2 groups of lysine, SH groups of cysteine, and OH groups of serine and tyrosine. Note that chlorogenic acid quinone can form protein adducts both at the acrylic acid side chain (adduct A) and on the benzene ring (adducts B, C) and that the carbon atom to which the protein becomes attached becomes asymmetric. In each case, the addition reaction can therefore create two diastereoisomers, analogous to the observed formation of LD- and LL-lysinoalanine isomers derived from addition of ϵ-NH_2 groups to the double bond of dehydroalanine (Friedman, 1977; Friedman and Pearce, 1989; Liardon et al., 1991). The nutritional and toxicological significance of consuming such protein derivatives is largely unknown.

Polyphenolic compounds and derivatives (tannins) bind to proteins in the gut, adversely affecting absorption of food in both insects and animals (Duffey and Stout, 1996; Friedman, 1989; Oste, 1989). Rat feeding studies (Griffiths, 1986) suggest that reduction in protein nutritional quality following consumption of polyphenols may be due to formation of protein−polyphenol complexes (Spencer et al., 1988) and to inhibition of the digestive enzymes α-amylase and trypsin. Polyphenols also induced an increase in lipase activity in the digestive system of the rats. However, unlike legume protease inhibitors (Gumbmann and Friedman, 1987), polyphenolic compounds did not induce pancreatic hypertrophy. Possible effects of polyphenol-rich diets on protein nutrition need to be better defined.

RESEARCH NEEDS

This integrated overview covers contributions from several overlapping disciplines with a common concern for theoretical and practical consequences of the function of potato polyphenols in the plant and in the diet. It will hopefully catalyze progress and permit the widest possible interations of viewpoints and expertise needed to find solutions to some of the above-mentioned problems. Such synergistic, mutually beneficial interaction will benefit both the farmer growing polyphenol-containing plant foods and the consumer who expects improved food quality, safety, and health. The following are some additional implications and research needs suggested by the described roles of potato polyphenols in the plant and in the diet.

The complex dynamics and the rate of compositional changes during storage of potatoes is affected by different storage conditions including light, temperature, and humidity and may be cultivar-related. A need exists to minimize adverse compositional changes during handling, sampling, storing, shipping, and marketing of potatoes. Specifically, storage studies with commercial and experimental cultivars should determine effects of light and other environmental factors on glycoalkaloid levels, polyphenol content (predictor of browning and other discolorations), chlorophyll content (greening), protease inhibitors and phytoalexins (resistance factors), and glucose and free amino acid content (indicators of nonenzymatic browning). Such information could serve as a guide for the industry to minimize postharvest changes in potatoes for various end uses and will help in the selection of specific potato cultivars showing the greatest resistance to stress-induced compositional changes. Since resistance to stress conditions including phytopathogens causing late blight may be due to glycoalkaloid, phytoalexin, polyphenol, and protease inhibitor content, the profiles of compositional changes of different cultivars will make it possible to evaluate full-spectrum resistance of a given line. Such profiles could serve as a guide to producing and marketing cultivars with increased resistance without the need for lengthy, large-scale field trials.

To minimize adverse effects of stress-induced changes during storage, a need also exists to develop specific indicators of stress. We recently discovered that the enzyme solanidine glucosyltransferase (SGT) is induced in wounded potato tubers and leaves by stress conditions such as slicing (Moehs et al., 1996a,b; 1997, Stapleton et al., 1991). Studies are needed to ascertain whether the level of SGT or of other enzymes such as epoxide hydrolase, which is induced by wounding (Stapleton et al., 1994), can be measured by a simple ELISA and whether such enzymes can serve as general indicators for postharvest bruising and blackspot formation, late blight, and other stress conditions in susceptible potato tubers.

A major concern of polyphenol research is whether phytochemicals such as chlorogenic acid behave differently, depending on whether they are consumed alone

or as part of a complex diet, which could affect their stability, interaction with other dietary components, and consequently their efficacy. Another concern, as noted elsewhere (Friedman and McDonald, 1997), is that plant breeding and molecular genetic studies designed to create improved potato cultivars need continuing guidance from compositional and safety evaluations to assure the safety of newly developed potatoes. Thus, the practical significance for host-plant resistance and for potato quality and nutrition of enzymic browning prevention through suppression of genes involved in the biosynthesis of polyphenol oxidase through antisense RNA (Bachem et al., 1994) is also worthy of study. Since preventing the biosynthesis of PPO may result in accumulation of monomeric polyphenols at the expense of polymeric ones, adverse effects on host-plant resistance in which polymeric compounds participate are a possibility. On the other hand, increased monomeric polyphenol content may have beneficial dietary consequences, as discussed earlier (Sim et al., 1997).

The preceding analysis of the current knowledge of potato polyphenols in the plant and in the diet shows that these studies constitute an evolving, potentially beneficial area of food science, food safety, and nutrition with many unsolved problems. In addition to recommendations made earlier, we are challenged to respond to additional research needs outlined below.

1. Assess whether antioxidative potencies of polyphenols, in terms of their abilities to trap damaging hydroxyl ($OH^{\bullet}$), alkoxyl ($RO^{\bullet}$), peroxyl ($RCOO^{\bullet}$), and superoxide anion ($O_2^{\bullet -}$) radicals, can be predicted from the net electrochemical redox potentials of mixtures of structurally different polyphenols actually present in potatoes and other plant foods.

2. Define relative health-promoting properties of structurally different chlorogenic acid isomers. Determine whether two or more polyphenols can act synergistically as antioxidants.

3. Enhance the content of the most potent antioxidative polyphenolic compounds in potatoes by plant breeding and plant molecular biology techniques.

4. Define effects of commercial and home food processing on polyphenols in potatoes.

5. Develop new, inexpensive, nutritious, and health-promoting high-chlorogenic acid potato tuber, peel, and leaf food formulations. The possible value of leaves as a food source deserves additional comment. Previously, major efforts were made to remove pigments in the preparation of edible leaf protein isolates (Bickoff et al., 1973; Pirie, 1973; Friedman, 1996a). Since leaves have a high polyphenol content (Tables 2 and 5) and since chlorophyll binds strongly to carcinogenic heterocyclic amines (Friedman, 1996b), it may be worthwhile to retain both of these leaf constituents in the preparation of the isolates.

6. Carry out animal and human feeding studies with high chlorogenic acid potato diets to assess whether beneficial effects of chlorogenic acid *in vitro* are confirmed *in vivo*.

The suggested research needs apply to chlorogenic acid-containing fruits and vegetables in general. All such studies are based on the assumption that there are significant concentrations of polyphenols in the edible portions of potatoes and other foods, as consumed. In addition, high chlorogenic acid potatoes would have to be acceptable to consumers with respect to blackspot, after-cooking darkening, and sensory qualities. The consumer may have to choose between perceived undesirable appearance and real beneficial health effects.

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