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**BROWNING OF FOODS:  
CONTROL BY SULFITES,  
ANTIOXIDANTS,  
AND OTHER MEANS**

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Expert Panel on Food Safety and Nutrition*

# Why Sulfite Alternatives?

**S**ULFITES WERE ONE OF THE first food additives to be used by humans. In the form of sulfur dioxide gas generated from the burning of sulfur, they were used to sanitize wine and cider vessels as early as the 17th century. Later, many other functional uses for sulfites in foods were identified. One could argue that sulfites are the most useful of all food ingredients because they can perform a myriad of functions in various foods.

Sulfites are widely used in wine making and the wet milling of corn to prevent undesirable microbial growth. They are also widely used to control or prevent the browning of foods: as noted in the Scientific Status Summary, "Browning of Foods: Control by Sulfites, Antioxidants, and Other Means" (pp. 75-84). In this capacity, sulfites are commonly used in dried fruits and vegetables, pre-peeled fresh potatoes for the foodservice industry, and shrimp. Until recent years, sulfites were also commonly used to prevent browning in other fresh fruit and vegetable applications; these uses are now banned for reasons noted below.

In many countries, although the practice is not common in the U.S., sulfites are also employed as antioxidants to diminish rancidity. In this regard, they are particularly useful as antioxidants in cured meats. Sulfites have numerous other beneficial properties that are critical in particular food applications: they can be effective dough conditioners to improve the texture of frozen dough products and are effective bleaching agents in the processing of maraschino cherries and hominy.

Sulfites have been considered safe and effective ingredients ever since their introduction into our food supply. The Food and Drug Administration has long considered sulfur dioxide and the sulfite, bisulfite, and metabisulfite salts of sodium and potassium to be Generally Recognized as Safe (GRAS). The Joint Expert Committee on Food Additives of the World Health Organization also considers sulfites safe for use in foods and has established an Acceptable Daily Intake of 42 mg/

day for a 60-kg human. So why search for alternatives when sulfites exhibit such a wide spectrum of useful properties, are considered safe, and are comparatively inexpensive?

**T**HE ANSWER BEGAN TO evolve in 1981. I will never forget the landmark event that triggered the current concerns about sulfites. I was attending my first American Academy of Allergy & Immunology meeting in March 1981 (I remain the only food scientist to routinely participate in this medical conference). I heard two separate reports by Drs. Don Stevenson and Ron Simon of Scripps Clinic in California and Dr. David Allen from Australia describing asthmatic reactions to sulfites. Sulfites are common additives in pharmaceutical products also, and most of the case reports involved adverse reactions to sulfites contained in medications, although homemade wine and restaurant salads were implicated in one case. I was probably the only person in the audience who recognized the potential widespread significance of these reports to the food industry.

Over the next few years, more case reports of sulfite-induced adverse reactions followed, and sulfited foods were implicated in many of these cases. Lettuce, cut fruit, and guacamole from restaurant salad bars were frequently implicated, and this illness became known as "The Salad Bar Syndrome." Ultimately, research revealed that only a few hundred thousand consumers in the entire U.S. were likely to be sulfite-sensitive.

Asthma remains the only well-documented adverse reaction associated with sulfite sensitivity, although only a small percentage of all asthmatics are sulfite-sensitive. Other symptoms have been reported in some cases, but a cause-and-effect relationship has not been clearly established. FDA has collected thousands of reports from consumers alleging sulfite-induced reactions, including more than 20 alleged deaths.

Asthma can, on occasion, be a life-threatening reaction, and it is quite likely that some consumers have died from ingestion of foods containing high levels of sulfite. The mechanism of sulfite-induced asthma remains unknown, although sulfite sensitivity is not a true allergic reaction.

The identification of sulfite sensitivity generated considerable concern from the food industry, consumers, the medical community, and regulatory agencies. In 1986, FDA revoked the GRAS status of sulfites for use on fresh fruits and vegetables other than potatoes. The use of sulfites on fruits and vegetables in foodservice salad bars was clearly triggering many of the adverse reactions, and this regulation was intended to halt that practice. At the same time, FDA also required that sulfited foods be labeled if detectable amounts of sulfite residues remained in the finished product.

These regulations have proven effective. Sulfite use in salad bars has been discontinued. Many of the sulfite alternatives discussed in the Scientific Status Summary were developed as replacements for sulfite for such applications. Sulfite-sensitive consumers can identify sulfited packaged foods by scrutinizing food labels. As a result, the number of reported adverse reactions to sulfites has dropped significantly, and I am unaware of any recently reported deaths.

**T**HESE CONCERNS AND REGULATIONS have also resulted in an intense interest in the identification of useful alternatives to allow the food industry to eliminate or reduce certain uses of sulfites. The challenge to develop equally effective alternatives is substantial, given the myriad useful functions of sulfites.

Many food products undergo browning due to enzymatic or nonenzymatic reactions that occur during processing and storage. Such reactions have an important bearing on food quality (good or bad) and are therefore of great importance to the food industry. Until recently, both enzymatic and nonenzymatic browning in foods could be inhibited by application of sulfites. However, sulfites have been associated with severe allergy-like reactions in some asthmatics, prompting the Food and Drug Administration (FDA) to limit them to certain categories of food products (FDA, 1986, 1990). Because of these restrictions, food processors have turned to a number of sulfite alternatives, mostly formulations effective only against enzymatic browning, with varying success. The demand for more effective browning inhibitors has stimulated considerable research activity in this area, resulting in the development of a number of promising new browning inhibitor treatments.

In this Scientific Status Summary, we will review essential differences between enzymatic and nonenzymatic browning that are pertinent to control of these discolorations, survey the current state of the art with regard to browning inhibitors, and examine the outlook for new approaches and improvements in control of browning. We will focus on the problem of controlling enzymatic browning in fruits, vegetables, and shellfish, since this is where most research activity has taken place, but we must also address the need to find effective treatments to control nonenzymatic browning as well.

### **BROWNING REACTIONS IN FOODS**

Browning discolorations in foods are more complex than is suggested by the simple classification of these reactions as enzymatic or nonenzymatic, because of the large number of secondary reactions that may occur. This is reflected in the range of colors produced by such reactions, even in the same commodity. For example, pre-peeled potatoes may develop red, brown, or even black discolorations, sometimes on opposite sides of the same tuber (Feinberg et al., 1987). These discolorations are the result of enzymatic browning reactions, but nonenzymatic "after-cooking darkening," induced by heating during steam or lye peeling, also may contribute to discoloration of the peeled surface (Smith, 1987a). Similarly, mushrooms undergoing enzymatic browning may develop pink, brown, black, gray, or even purple stains, in some cases, by reactions that are poorly understood (Nichols, 1985). Discolorations may occur in some raw products in which endogenous or added ascorbic acid (AA) is oxidized to dehydroascorbic acid (DHAA), which then reacts with amino acids to yield brown colors by the Maillard reaction or other nonenzymatic means (Kacem et al., 1987).

**Enzymatic Browning.** Enzymatic browning is the discoloration that results when monophenolic compounds of plants or shellfish, in the presence of atmospheric oxygen and polyphenol oxidase (PPO), are hydroxylated to *o*-diphenols, and the latter are oxidized to *o*-quinones (Mayer and Harel, 1979; Vamos-Vigyazo, 1981; McEvily et al., 1992). PPO (E.C 1.14.18.1), is also known as tyrosinase, *o*-diphenol oxidase, catechol oxidase, etc. The quinones condense and react nonenzymatically with other phenolic compounds, amino acids, etc., to produce

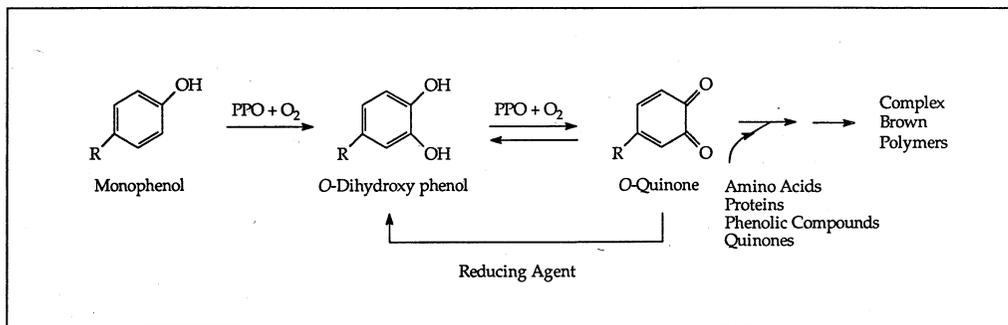


Fig. 1—Enzymatic Browning Reaction, showing action of reducing agents as browning inhibitors. Adapted from McEvily et al. (1992)

pigments of indeterminate structure (Fig. 1). A variety of phenolic compounds are oxidized by PPO; the most important substrates are catechins, cinnamic acid esters, 3,4-hydroxyphenyl-alanine (DOPA), and tyrosine. The optimum pH for PPO activity is between pH 5 and 7. The enzyme is relatively heat labile and can be inhibited by acids, halides, phenolic acids, sulfites, chelating agents, reducing agents such as ascorbic acid, quinone couplers such as cysteine, and various substrate-binding compounds.

Enzymatic browning is a significant problem in a number of important commodities, specifically fruits such as apples, pears, peaches, bananas, and grapes; vegetables such as potatoes, mushrooms, and lettuce; and seafoods such as shrimp, spiny lobsters, and crabs. This discoloration limits the shelf life of many minimally processed foods (Huxsoll et al., 1989) and also may be a problem in the production of dehydrated and frozen fruits and vegetables (Shewfelt, 1986; Hall, 1989).

Enzymatic browning is not always a defect; this reaction contributes to the desirable color and flavor of such products as raisins, prunes, coffee, tea, and cocoa (Mayer and Harel, 1979; Vamos-Vigyazo, 1981).

Enzymatic browning can be controlled in some fruit and vegetable

products by blanching to inactivate PPO (Hall, 1989; McCord and Kilara, 1983; Ma et al., 1992). Blanching cannot be used with some products, however, since it would adversely affect flavor and texture. Consequently, other approaches such as the exclusion of oxygen and/or application of browning inhibitors must be used.

**Nonenzymatic Browning.** Discolorations resulting from the reaction of carbonyl and free amino groups that lead to the formation of brown melanoidin pigments—i.e., the classic Maillard reaction (Fig. 2)—limit the shelf life of various dehydrated fruits and vegetables, citrus products, and juices (Hodge, 1953; Labuza and Schmidl, 1986; Handwerk and Coleman, 1988). Although nonoxidative

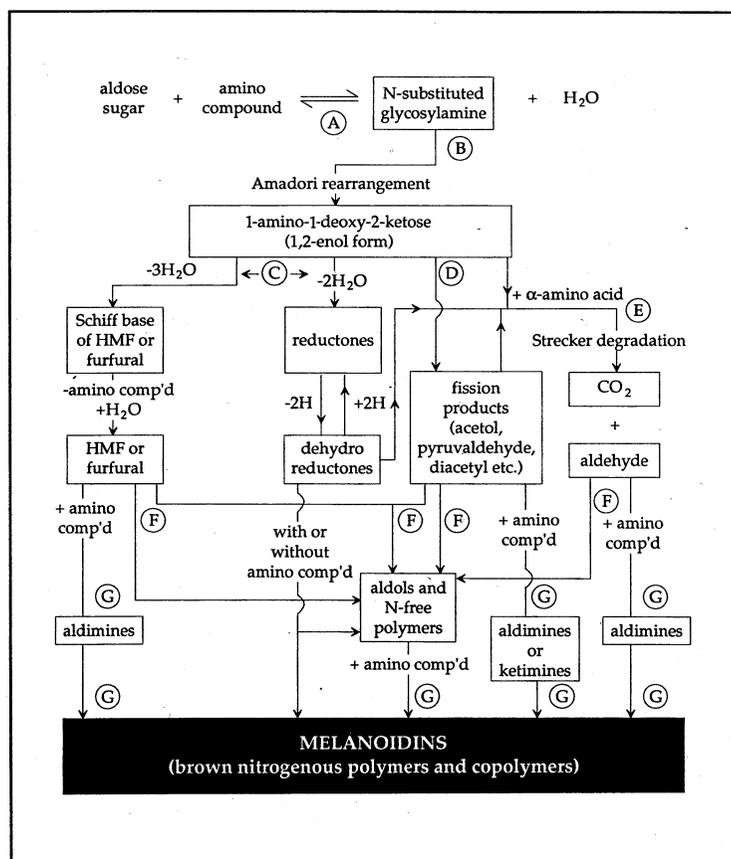


Fig. 2—Nonenzymatic Browning Reaction (Maillard Reaction). A, sugar-amine condensation; B, Amadori rearrangement; C, sugar dehydration; D, sugar fragmentation; E, Strecker degradation of amino acid moiety; F, aldol condensation; G, aldehyde-amine polymerization and formation of heterocyclic nitrogen compounds. From Hodge (1953)

browning reactions between reducing sugars and amino acids or proteins are important in many products, browning also may result from sugar degradation (Lee and Nagy, 1988) or from the oxidative degradation of ascorbic acid and further reaction of the carbonyl compounds formed via aldol condensation or reaction with amino groups to yield brown pigments (Kacem et al., 1987; Wong and Stanton, 1989; Löscher et al., 1991). Phenolic compounds also can undergo non-enzymatic oxidations to yield brown pigments (Cilliers and Singleton, 1989). These reactions have been the subject of numerous reviews (Waller and Feather, 1983; Handwerk and Coleman, 1988; Namiki, 1988) and will not be discussed further, except in relation to the use of sulfites and other browning inhibitors.

In addition to causing discoloration, non-enzymatic browning reactions also result in destruction of nutrients such as essential amino acids and ascorbic acid, reduced protein digestibility, inhibition of digestive enzymes, and interference with mineral metabolism through metal ion complexation. Potentially toxic and mutagenic Maillard reaction products also may be formed, especially in cooked muscle foods (Namiki, 1988; O'Brien and Morrissey, 1989).

While nonenzymatic browning is a defect in some products, it is a desirable attribute in others such as bakery products, snack foods, nuts, and roasted meats. To compensate for the lack of color development during microwave cooking of certain foods, browning precursors may be incorporated into the product to induce browning during microwave heating (Fellenz and Moppett, 1991). Volatiles produced by non-enzymatic browning reactions during cooking contribute to the flavor of many foods (Bailey, 1983; Whitfield, 1992).

The extent of nonenzymatic browning in foods depends on product composition, e.g., Maillard precursors or ascorbic acid (Wong and Stanton, 1989; Kennedy et al., 1990); pH (Wedzicha and Goddard, 1988; O'Brien and Morrissey, 1989); water activity (Monsalve et al., 1990); exposure to oxygen (Kacem et al., 1987); and storage time and temperature (Nagy et al., 1990).

Nonenzymatic browning in fruit and vegetable products can be inhibited by refrigeration; control of water activity in dehydrated foods (Labuza and Saltmarch, 1981); reduction of reducing-sugar content in potatoes by storage (Smith, 1987b), or glucose oxidase treatment (Low et al., 1989); reduction of amino nitrogen content in juices by ion exchange (Norman, 1990); packaging with oxygen scavengers; and use of sulfites (Bolin and

Steele, 1987). Sulfhydryl-containing amino acids were nearly as effective as bisulfite in inhibiting nonenzymatic browning in a model system (Friedman and Molnar-Perl, 1990). However, cysteine treatment was ineffective in dried apple (Bolin and Steele, 1987).

#### SULFITES AS BROWNING INHIBITORS

Sulfites are highly effective in controlling browning but are subject to regulatory restrictions because of adverse effects on health.

**Sulfite Treatments.** Sulfiting agents (sulfur dioxide, sodium sulfite, sodium and potassium bisulfites and metabisulfites) have been added to many foods since antiquity to prevent enzymatic and nonenzymatic browning; control growth of microorganisms; act as bleaching agents, antioxidants, or reducing agents; and carry out various other technical functions (Taylor et al., 1986). Sulfites act as PPO inhibitors and also react with intermediates to prevent pigment formation (Sayavedra-Soto and Montgomery, 1986). Sulfites inhibit nonenzymatic browning by reacting with carbonyl intermediates, thereby preventing their further reaction to form brown pigments (Wedzicha, 1987).

Sulfite treatment levels in foods vary widely, depending on the application. Residual levels usually do not exceed several hundred parts per million but may approach 1,000 ppm in certain fruit and vegetable products (Taylor et al., 1986). FDA has proposed that maximum residual sulfur dioxide levels of 300, 500, and 2,000 ppm be permitted in fruit juices, dehydrated potatoes, and dried fruit, respectively (FDA, 1988b).

**Safety Issues.** In response to its 1982 proposal (FDA, 1982) to affirm the Generally Recognized as Safe (GRAS) status of sulfiting agents, FDA received reports of adverse allergic-type reactions that were attributed to the consumption of foods containing sulfites. These reports indicated that sulfites can induce asthmatic episodes in a segment of the asthmatic population. In rare cases, severe asthmatic or even anaphylactic-like reactions may occur (Taylor et al., 1986).

At FDA's request, the Federation of American Societies for Experimental Biology (FASEB) established an ad hoc review panel in 1984 to reexamine the GRAS status of sulfiting agents. In its final report (FASEB, 1985), this panel concluded that sulfiting agents are not teratogenic, mutagenic, or carcinogenic in laboratory animals. The panel found no new metabolic or toxicological data that suggested a need to change the no-observed-adverse-effect level, which is about ten times the level of sulfur

dioxide ingested by high-intake (99th percentile) consumers and 180 times the mean per capita daily intake. They concluded that "For the majority of the population, there is no evidence . . . that demonstrates or suggests reasonable grounds to suspect a hazard to the public when these substances (sulfiting agents) are used at levels that are now current. . . ." The panel also concluded that "For the fraction of the public that is sulfite sensitive, there is evidence in the available information on [sulfiting agents] that demonstrates or suggests reasonable grounds to suspect a hazard of unpredictable severity to such individuals . . ." (FDA, 1988b).

**Regulatory Issues.** In 1959, sulfiting agents were listed as GRAS for use as chemical preservatives. In response to significant questions raised about the safety of these food ingredients, FDA in 1986 revoked the GRAS status of sulfites in fruits and most vegetables intended to be served raw or sold raw to consumers (FDA, 1986). In March 1990, FDA extended this revocation to "fresh potatoes served or sold unpackaged and unlabeled to consumers" (FDA, 1990), but this revocation was reversed in a decision of the U.S. Court of Appeals for the 3rd Circuit in Philadelphia on May 22, 1991 (Anonymous, 1991).

New rules, proposed by FDA in 1988, required that the presence of sulfites in standardized foods be declared on the label when the sulfiting agents have a functional effect or are present at a detectable level, defined as 10 ppm or more (FDA, 1988a). Additional rules affirmed the GRAS status of sulfiting agents in certain specified foods at specified maximum residual levels, provided that the presence of sulfite is declared on the label of packaged products or on bulk containers "plainly in view" of the purchaser or is indicated by a counter sign, card, or other device bearing information that the product has been treated with sulfites. Sulfiting agents are not GRAS for use in meats, foods recognized as a major source of vitamin B-1, or "fruits or vegetables intended to be served raw to consumers or sold raw to consumers or to be presented to consumers as fresh" (FDA, 1988b).

#### ALTERNATIVES TO SULFITES

FDA restrictions on the use of sulfites in certain fruit and vegetable products and concern that other uses might be subject to future limitations have prompted researchers and ingredient suppliers to develop sulfite substitutes (Sapers and Hicks, 1989). Sulfites are multifunctional agents. The search for alternatives has yielded compounds that are effective substitutes for only one or two of the functionalities obtained with sulfites. It is unlikely that a multifunctional sulfite substitute can be developed. Rather,

combinations of several active ingredients, formulated to meet the needs of specific commodities and product types will be developed. Such formulations must be cost-effective in their stated use (although not necessarily equivalent to sulfite in cost or effectiveness), and they must be approved for food use by FDA.

**Ascorbic Acid-Based Formulations.** Probably the best known alternative to sulfite is ascorbic acid (vitamin C). This compound is a highly effective inhibitor of enzymatic browning, primarily because of its ability to reduce quinones, generated by PPO-catalyzed oxidation of polyphenols, back to phenolic compounds before they can undergo further reaction to form pigments (Fig. 1). However, once added ascorbic acid has been completely oxidized to DHAA by this reaction, quinones can accumulate and undergo browning. Additionally, as discussed previously, DHAA itself can brown non-enzymatically. At high concentrations, ascorbic acid also can directly inhibit PPO (Vamos-Vigyazo, 1981).

Ascorbic acid and its isomer erythorbic (*d*-isoascorbic) acid have been used for almost 50 years as inhibitors of enzymatic browning in fresh-cut and frozen fruits such as peaches and apples (Tressler and DuBois, 1944; Esselen et al., 1945). These compounds are added to syrups or applied by dipping the fruit in solutions containing the browning inhibitor, sometimes in combination with an organic acid such as citric acid and a calcium salt. Browning-inhibitor penetration can be enhanced by vacuum infiltration of treatment solutions, which also removes air from within the product's void spaces (Guadagni, 1949).

More recent interest in sulfite substitutes, in response to proposed regulatory action by FDA, has produced a proliferation of browning-inhibitor products. A tabulation made in 1986 by the National Restaurant Association listed 13 suppliers of such formulations. These products generally contain ascorbic acid or erythorbic acid, or their sodium salts, usually in combination with one or more adjuncts such as citric acid or some other acidulant, a calcium salt, a phosphate, sodium chloride, cysteine, or a preservative such as sodium benzoate or potassium sorbate.

Since 1986, additional browning-inhibitor formulations have been marketed (Langdon, 1987; Cherry and Singh, 1990; Gardner et al., 1991; Warren, 1991). The proportions of ingredients in these formulations is proprietary information. However, the total use levels recommended by their suppliers for similar applications vary widely, as do recommended use levels and proportions of

ascorbic acid and citric acid in browning-inhibitor formulations. Thus, there appears to be no consensus as to optimal ascorbic acid level for treatment of fruits and vegetables.

Browning-inhibitor suppliers are in general agreement that the storage life of treated fresh commodities is 4-7 days. A longer storage life can be obtained with pre-peeled potatoes by shipping them in a preservative solution following treatment with erythorbic acid (Santerre et al., 1991) or by vacuum packing treated potatoes to exclude oxygen (Langdon, 1987). However, products protected by vacuum packing will brown rapidly once the consumer has opened the package. Furthermore, there is a safety concern about vacuum packaging pre-peeled potatoes in a high-barrier film because of the potential for *Clostridium botulinum* to grow and produce toxin under anaerobic conditions (Tammenga et al., 1978).

Ascorbic acid-based browning inhibitors are usually not as effective as sulfites because of the greater stability and better penetration of the latter. Stable derivatives of ascorbic acid have been substituted for ascorbic acid in experimental formulations. Use of ascorbic acid-2-phosphates in browning-inhibitor formulations for apples and potatoes can significantly improve their performance (Sapers et al., 1989b; Sapers and Miller, 1992). Ascorbyl palmitate and other fatty acid esters of ascorbic acid are effective with fruit juices (Sapers et al., 1989b). With the exception of ascorbyl palmitate, these derivatives have not yet been approved for food use by FDA. Another derivative,  $\alpha$ -glucosyl ascorbic acid may show greater stability than ascorbic acid and be suitable for use as a browning inhibitor in systems where sufficient levels of  $\alpha$ -glucosidase are present (Ikai, 1990).

The penetration of ascorbic acid-based browning inhibitors can be improved by treating under pressure or vacuum instead of dipping or spraying (Sapers et al., 1990). However, excessive absorption of browning-inhibitor solution by treated samples will result in a water-logged appearance and premature spoilage of fresh commodities.

**PPO Inhibitors.** Many inhibitors of PPO are known, but only a few have been considered as potential alternatives to sulfites (Vamos-Vigyazo, 1981). Cinnamic acid and benzoic acid were found to be effective in apple juice, especially when used in combination with ascorbic acid (Walker, 1976; Sapers et al., 1989b). These inhibitors also were effective when applied to cut surfaces of apples, but induced browning under some circumstances. Carbon monoxide has been proposed as a browning inhibitor for mushrooms

(Albisu et al., 1989). Use of this compound in a modified-atmosphere packaging system would require measures to ensure the safety of packing-plant workers. 4-Hexylresorcinol is the active ingredient in Everfresh™, a browning inhibitor being used on shrimp. This compound has been proposed for use on various fruits and vegetables by McEvily et al. (1991a, b). These investigators consider this compound to be effective and safe, since it has had a long history of human consumption (Frankos et al., 1991).

Kojic acid [5-hydroxy-2-(hydroxymethyl)- $\gamma$ -pyrone], a fungal metabolite, has been shown to be a PPO inhibitor, acting by interfering with oxygen uptake and by reducing *o*-quinones to diphenols to prevent pigment formation (Chen et al., 1991). Whether this compound shows potential as a practical browning inhibitor is not clear, especially in light of its mutagenic properties (Wei et al., 1990).

**Complexing Agents.** Since copper is essential to the function of PPO, chelating agents that complex copper may have value as browning inhibitors. Ethylenediamine tetraacetic acid (EDTA), a widely used chelating agent, is not very effective as an inhibitor of peach PPO (Wong et al., 1971) and does not inhibit browning in apple slices (Sapers, 1986). This compound and sodium acid pyrophosphate are used to control after-cooking darkening in pre-peeled potato (Feinberg et al., 1987). Citric acid, an ingredient in many browning-inhibitor formulations, acts as a chelating agent and acidulant, both functionalities inhibiting PPO (McCord and Kilara, 1983; Santerre et al., 1988). Sporix, a chelating agent described by its supplier as an acidic polyphosphate, has been found to be an effective browning inhibitor in several fruits and vegetables (Friedman, 1986; Gardner et al., 1991). This compound has not yet been approved for food use by FDA.

Compounds that bind or complex PPO substrates also may have potential value as browning inhibitors. Polyvinylpyrrolidone (PVPP), a product permitted for use as a fining agent for apple juice, can bind polyphenols and prevent their participation in enzymatic browning reactions (Van Buren, 1989). Similarly, cyclodextrins (cyclic polysaccharides) can form inclusion complexes with polyphenol substrates of PPO. Addition of soluble cyclodextrins to juices or treatment of juices in insoluble cyclodextrin columns can prevent browning (Sapers et al., 1989b). Cyclodextrins have not yet been approved for food use by FDA. However, a company planning to use  $\beta$ -cyclodextrin to remove cholesterol from egg yolk has petitioned FDA for affirmation

of GRAS status for this application (FDA, 1992).

**Sulfhydryl-Containing Amino Acids.** The ability of cysteine to inhibit PPO has been recognized for many years. Cysteine prevents brown pigment formation by reacting with quinone intermediates to form stable, colorless compounds (Dudley and Hotchkiss, 1989). Cysteine has been used as an ingredient in a commercial browning inhibitor (Cherry and Singh, 1990). Recent studies suggest that reduced glutathione and N-acetylcysteine are nearly as effective as sulfites in controlling browning in apple, potato, and fresh fruit juices (Molnar-Perl and Friedman, 1990a, b).

**Other Browning Inhibitors.** Inorganic halides are well-known inhibitors of PPO (Vamos-Vigyazo, 1981), and sodium chloride is a component of some commercial browning inhibitors. Use of this compound is GRAS but limited by its effect on product taste. Zinc chloride has been shown to be a highly effective browning inhibitor, especially when used in combination with calcium chloride, ascorbic acid, and citric acid (Bolin and Huxsoll, 1989).

Treatment of white grapes and cut fruit with honey has been shown to inhibit enzymatic browning. This effect appears to be due to the presence in honey of a small peptide having a molecular weight of about 600 Da rather than to a reduction in dissolved oxygen due to the added sucrose. Research on the characterization of this natural inhibitor and its practical application are in progress (Oszmianski and Lee, 1990).

An edible coating was reported to prevent enzymatic browning of mushroom slices (Nisperos-Carriedo et al., 1991). Various sulfated polysaccharides including carrageenans, amylose sulfate, and xylan sulfate, were found to be effective as browning inhibitors with apple juice and diced apple (Tong and Hicks, 1991). Dips containing ascorbic acid and a thixotropic gum, such as xanthan, have been used to extend the shelf life of fruits and vegetables used in salad bars and prepared salads (Wyss et al., 1990). Such dips may coat the fruit or vegetable with an oxygen-impermeable barrier and/or increase the amount of ascorbic acid retained by the product after dipping. Further research on these inhibitors and other active polysaccharides is in progress.

Protease enzymes were claimed to be effective browning inhibitors for apples, potatoes, and shrimp (Taoukis et al., 1990; Labuza et al., 1992; Luo et al., 1992). The PPO activity of plum juice was significantly reduced when the juice was passed through a column containing immobilized proteases (Arnold et al., 1992). Further research is required

before this technology can be applied.

A protease-free extract from fig latex was reported to contain a component of less than 5,000 Da which inhibited enzymatic browning (McEvily, 1991).

**Exclusion of Oxygen.** Since oxygen is required for enzymatic browning to take place, this reaction can be inhibited by excluding oxygen from contact with the product. This was done more than 50 years ago by vacuum filling sliced fruits with syrup, sometimes containing ascorbic acid (Guadagni, 1949). While this approach is effective with products to be frozen, it would not be applicable to slices preserved by refrigeration, since they would become objectionably water-logged (Ponting and Jackson, 1972; Sapers et al., 1990).

Oxygen concentrations in the atmosphere surrounding a product such as shredded lettuce or mushrooms can be reduced by modified-atmosphere packaging. While this approach can delay browning, excessive reduction of oxygen will damage the product by inducing anaerobic metabolism, leading to breakdown and off-flavor formation (Ballantyne et al., 1988). The removal of oxygen also entails a risk that conditions in the product might become favorable for the growth of *Clostridium botulinum*. To avoid such a risk, overwrapped packages of fresh mushrooms must contain holes admitting air so that this product, which has a high respiration rate, will not become anaerobic (Nichols, 1985).

**Other Alternatives.** Ultrafiltration has been studied, with mixed results, as an alternative to sulfiting white wine (Sims et al., 1989; Goodwin and Morris, 1991). Presumably, the ultrafiltration membrane will remove PPO but not lower-molecular-weight polyphenols or Maillard-reaction precursors which could undergo nonenzymatic browning during storage. Addition of nisin to wine to control malolactic fermentation may reduce the amount of sulfur dioxide used to control bacterial spoilage (Daeschel et al., 1991). Alternatively, sulfites might be removed from wine by ion exchange and treatment with carbon (Brown, 1991).

The severity of enzymatic browning at cut or peeled surfaces of fruits and vegetables will depend in part on the extent of damage done to surface tissues by the peeling or cutting procedure. Peeling potatoes with a sharp knife is less injurious than peeling by abrasion or steam (Sapers et al., 1989a). A water-jet cutting system was found to produce more subsurface cellular damage in sliced potato than a sharp knife blade, as judged by scanning electron microscopic observation and measurement of protein

extractability at the cut surface (Becker and Gray, 1992).

Different cultivars of fruits and vegetables may show large differences in their tendency to brown, because of cultivar variation in PPO activity and substrate content. Empire and Granny Smith apples (Coseteng and Lee, 1987; Sapers and Douglas, 1987) and Atlantic potato (Sapers et al., 1989a) are examples of cultivars that brown slowly. Such differences can be exploited by selecting raw materials for processing that have a low tendency to brown so that treatments to control browning can be minimized. Genetic engineering as well as conventional plant-breeding methods may be useful in developing low-browning fruits and vegetables.

## CONCLUSIONS

Treatment of fruits and vegetables with sulfites is the most effective means available today to control browning. However, because sulfites have been banned in certain categories of products and their regulatory status for other categories is in question, the food industry is looking for alternative means of controlling browning. Some applications of sulfite are not at risk of banning, since treatment residues—the source of adverse reactions—vary greatly with commodity, method of processing, and method of preparation by consumers.

Current alternatives to sulfites are not always equivalent to sulfites in effectiveness, cost, or functionality. However, the food industry can adapt to the use of sulfite alternatives by modifying processing conditions, product distribution, shelf-life specifications, or pricing. Such compromises eventually may be obviated by new developments and improvements in sulfite alternatives.

New approaches to controlling enzymatic browning are under study at university, government, and industry laboratories, and a number of interesting developments have resulted. These alternatives must be evaluated on the basis of effectiveness, cost, and regulatory status.

Because sulfites serve multiple functions in foods, e.g., inhibiting enzymatic browning, inhibiting nonenzymatic browning, and controlling growth of microorganisms, a sulfite replacement is likely to contain several components having different and complementary functions. The greatest need at this time is for the development of more effective inhibitors of nonenzymatic browning, since there are fewer effective options than with enzymatic browning. The compatibility of such formulations with the product must be considered carefully when designing sulfite alternatives. Inhibitors of

enzymatic browning must not affect product flavor or texture, induce leakage from cut surfaces, or promote nonenzymatic browning during product storage.

By encouraging the development of more effective inhibitors of enzymatic and nonenzymatic browning, the food industry should be able to minimize the impact of any future restrictions in the use of sulfites.

## REFERENCES

- Albisu, I., King, R.D., and Kozlov, I.A. 1989. Inhibition of the catecholase activity of mushroom tyrosinase by carbon monoxide. *J. Agric. Food Chem.* 37: 775-776.
- Anonymous. 1991. Report of decision by U.S. Court of Appeals for the 3rd Circuit. *Food Chemical News* 33(13): 2, May 27.
- Arnold, J.F., Sinha, N.K., and Cash, J.N. 1992. Effect of immobilized proteases on polyphenol oxidase inhibition and associated degradation of anthocyanins in plum juice. Presented at 1992 Annual Meeting, Inst. of Food Technologists, New Orleans, La., June 20-24.
- Bailey, M.E. 1983. The Maillard reaction and meat flavor. In "The Maillard Reaction in Foods and Nutrition," ed. G.R. Waller and M.S. Feather, ACS Symp. Series 215, pp. 169-184. Am. Chem. Soc., Washington, D.C.
- Ballantyne, A., Stark, R., and Selman, J.D. 1988. Modified atmosphere packaging of shredded lettuce. *Intl. J. Food Sci. Technol.* 23: 267-274.
- Becker, R. and Gray, G.M. 1992. Evaluation of a water jet cutting system for slicing potatoes. *J. Food Sci.* 57: 132-137.
- Bolin, H.R. and Huxsoll, C.C. 1989. Storage stability of minimally processed fruit. *J. Food Proc. Preserv.* 13: 281-292.
- Bolin, H.R. and Steele, R.J. 1987. Nonenzymatic browning in dried apples during storage. *J. Food Sci.* 52: 1654-1657.
- Brown, S.T. 1991. Method of removing sulfites from standard wine. U.S. patent 5,071,664.
- Chen, J.S., Wei, C-I., and Marshall, M.R. 1991. Inhibition mechanism of kojic acid on polyphenol oxidase. *J. Agric. Food Chem.* 39: 1897-1901.
- Cherry, J. and Singh, S.S. 1990. Discoloration preventing food preservative and method. U.S. patent 4,937,085.
- Cilliers, J.J.L. and Singleton, V.L. 1989. Nonenzymatic autoxidative phenolic browning reactions in a caffeic acid model system. *J. Agric. Food Chem.* 37: 890-896.
- Coseteng, M.Y. and Lee, C.Y. 1987. Changes in apple polyphenoloxidase and polyphenol concentrations in relation to degree of browning. *J. Food Sci.* 52: 985-989.
- Daeschel, M.A., Jung, D.-S., and Watson, B.T. 1991. Controlling wine malolactic fermentation with nisin and nisin-resistant strains of *Leuconostoc oenos*. *Appl. Environ. Microbiol.* 57: 601-603.
- Dudley, E.D. and Hotchkiss, J.H. 1989. Cysteine as an inhibitor of polyphenol oxidase. *J. Food Biochem.* 13: 65-75.
- Esselen, W.B. Jr., Powers, J.J., and Woodward, R. 1945. *d*-Isoascorbic acid as an antioxidant. *Ind. Eng. Chem.* 37: 295-299.
- FASEB. 1985. The reexamination of the GRAS status of sulfiting agents. Select committee on GRAS substances. Life Sciences Research Office, Federation

- of American Societies for Experimental Biology. Prepared under FDA contract 223-83-2020, Jan. 28.
- FDA. 1982. Sulfiting agents; Proposed affirmation of GRAS status with specific limitations; Removal from GRAS status as direct human food ingredient. Food and Drug Admin., Fed. Reg. 47: 29956.
- FDA. 1986. Sulfiting agents; Revocation of GRAS status for use on fruits and vegetables intended to be served or sold raw to consumers. Food and Drug Admin., Fed. Reg. 51: 25021-25026.
- FDA. 1987. Sulfiting agents; Proposal to revoke GRAS status for use on "fresh" potatoes served or sold unpackaged and unlabeled to consumers. Food and Drug Admin., Fed. Reg. 52: 46968-46978.
- FDA. 1988a. Sulfiting agents in standardized foods; Labeling requirements. Food and Drug Admin., Fed. Reg. 53: 51062-51065.
- FDA. 1988b. Sulfiting agents; Affirmation of GRAS status. Food and Drug Admin., Fed. Reg. 53: 51065-51084.
- FDA. 1990. Sulfiting agents; Revocation of GRAS status for use on "fresh" potatoes served or sold unpackaged or unlabeled to consumers. Food and Drug Admin., Fed. Reg. 55: 9826-9833.
- FDA. 1992. Michael Foods, Inc.; Filing of petition for affirmation of GRAS status. Food and Drug Admin., Fed. Reg. 57: 10767.
- Feinberg, B., Olson, R.L., and Mullins, W.R. 1987. Prepeeled potatoes. In "Potato Processing," 4th ed., ed W.F. Talburt and O. Smith, pp. 697-726. AVI-Van Nostrand Reinhold, New York.
- Fellenz, D.C. and Moppett, F.K. 1991. Browning agent enhances visual appeal of microwaved foods. Food Technol. 45(6): 111.
- Frankos, V.H., Schmitt, D.F., Haws, L.C., McEvily, A.J., Iyengar, R., Miller, S.A., Munro, I.C., Clydesdale, F.M., Forbes, A.L., and Sauer, R.M. 1991. Generally recognized as safe (GRAS) evaluation of 4-hexylresorcinol for use as a processing aid for prevention of melanosis in shrimp. Reg. Toxicol. Pharmacol. 14: 202-212.
- Friedman, M. and Molnar-Perl, I. 1990. Inhibition of browning by sulfur amino acids. 1. Heated amino acid-glucose systems. J. Agric. Food Chem. 38: 1642-1647.
- Friedman, S. 1986. Personal communication. International Sourcing, Inc. South Ridgewood, N.J.
- Gardner, J., Monohar, S., and Borisenok, W.S. 1991. Method and composition for preserving fresh peeled fruits and vegetables. U.S. patent 4,988,523.
- Goodwin, C.O. and Morris, J.R. 1991. Effect of ultrafiltration on wine quality and browning. Am. J. Enol. Viticulture 42: 347-353.
- Guadagni, D.G. 1949. Sirup treatment of apple slices for freezing preservation. Food Technol. 3: 404-408.
- Hall, G.C. 1989. Refrigerated, frozen and dehydrofrozen apples. In "Processed Apple Products," ed. D.D. Downing, pp. 239-256. AVI-Van Nostrand Reinhold, New York.
- Handwerk, R.L. and Coleman, R.L. 1988. Approaches to the citrus browning problem. A review. J. Agric. Food Chem. 36: 231-236.
- Hodge, J.E. 1953. Dehydrated foods: Chemistry of browning reactions in model system. J. Agric. Food Chem. 1: 928-943.
- Huxsoll, C.C., Bolin, H.R., and King, A.D. Jr. 1989. Physicochemical changes and treatments for lightly processed fruits and vegetables. In "Quality Factors of Fruits and Vegetables. Chemistry and Technology," ed. J.J. Jen, ACS Symp. Series 405, pp. 203-215. Am. Chem. Soc., Washington, D.C.
- Ikai, I. 1990. Personal communication. Hayashibara Biochemical Laboratories, Inc., Okayama, Japan.
- Kacem, B., Cornell, J.A., Marshall, M.R., Shireman, R.B., and Matthews, R.F. 1987. Nonenzymatic browning in aseptically packaged orange drinks: Effect of ascorbic acid, amino acids and oxygen. J. Food Sci. 52: 1668-1672.
- Kennedy, J.F., Rivera, Z.S., Lloyd, L.L., Warner, F.P., and Jumel, K. 1990. Studies on non-enzymatic browning in orange juice using a model system based on freshly squeezed orange juice. J. Sci. Food Agric. 52: 85-95.
- Labuza, T.P. and Saltmarch, M. 1981. The nonenzymatic browning reaction as affected by water in foods. In "Water Activity: Influence on Food Quality," ed. L.B. Rockland and G.F. Stewart, pp. 605-650. Academic Press, New York.
- Labuza, T.P. and Schmidl, M.K. 1986. Advances in the control of browning reactions in foods. In "Role of Chemistry in the Quality of Processed Food," ed. O.R. Fennema, W.H. Chang, and C.Y. Lii, p. 65. Food & Nutrition Press, Inc., Westport, Conn.
- Labuza, T.P., Lillemo, J.H., and Taoukis, P.S. 1992. Inhibition of polyphenoloxidases by proteolytic enzymes. Flüssiges Obst. 59: 15-20.
- Langdon, T.T. 1987. Prevention of browning in fresh prepared potatoes without the use of sulfiting agents. Food Technol. 41(5): 64-67.
- Lee, H.S. and Nagy, S. 1988. Relationship of sugar degradation to detrimental changes in citrus juice quality. Food Technol. 42(11): 91-97.
- Löscher, J., Kroh, L., Westphal, G., and Vogel, J. 1991. L-Ascorbic acid--a carbonyl component of non-enzymatic browning reactions. 2. Amino-carbonyl reactions of L-ascorbic acid. Z. Lebensm. Unters Forsch. 192: 323-327.
- Low, N., Jiang, Z., Ooraikul, B., Dokhani, S., and Palcic, M.M. 1989. Reduction of glucose content in potatoes with glucose oxidase. J. Food Sci. 54: 118.
- Luo, Y., Patterson, M.E., and Swanson, B.G. 1992. Scanning electron microscopy structure and firmness of papain treated apple slices. Food Structure 11: 333-338.
- Ma, S., Silva, J.L. Hearnberger, J.O., and Garner, J.O. Jr. 1992. Prevention of enzymatic darkening in frozen sweet potatoes [*Ipomoea batatas* (L.) Lam.] by water blanching: Relationship among darkening, phenols, and polyphenol oxidase activity. J. Agric. Food Chem. 40: 864-867.
- Mayer, A.M. and Harel, E. 1979. Polyphenol oxidases in plants. Phytochemistry 18: 193-215.
- McCord, J.D. and Kilara, A. 1983. Control of enzymatic browning in processed mushrooms (*Agaricus bisporus*). J. Food Sci. 48: 1479-1483.
- McEvily, A.J. 1991. Method of preventing browning of food utilizing protease free latex extracts particularly from figs. U.S. patent 4,981,708.
- McEvily, A.J., Iyengar, R., and Gross, A. 1991a. Compositions and methods for inhibiting browning in foods using resorcinol derivatives. U.S. patent 5,059,438.
- McEvily, A.J., Iyengar, R., and Otwell, S. 1991b. Sulfite alternative prevents shrimp melanosis. Food Technol. 45(9): 80-86.
- McEvily, A.J., Iyengar, R., and Otwell, W.S. 1992. Inhibition of enzymatic browning in foods and beverages. Crit. Rev. Food Sci. Nutr. 32: 253-273.
- Molnar-Perl, I. and Friedman, M. 1990a. Inhibition of browning by sulfur amino acids. 2. Fruit

- juices and protein-containing foods. *J. Agric. Food Chem.* 38: 1648-1651.
- Molnar-Perl, I. and Friedman, M. 1990b. Inhibition of browning by sulfur amino acids. 3. Apples and potatoes. *J. Agric. Food Chem.* 38: 1652-1656.
- Monsalve, A., Powers, J.R., and Leung, H.K. 1990. Browning of dehydroascorbic acid and chlorogenic acid as a function of water activity. *J. Food Sci.* 55: 1425-1428.
- Nagy, S., Lee, H., Rouseff, R.L., and Lin, J.C.C. 1990. Nonenzymatic browning of commercially canned and bottled grapefruit juice. *J. Agric. Food Chem.* 38: 343-346.
- Namiki, M. 1988. Chemistry of Maillard reaction; Recent studies on the browning reaction mechanism and the development of antioxidants and mutagens. *Adv. Food Res.* 32: 115-184.
- Nichols, R. 1985. Post-harvest physiology and storage. In "The Biology and Technology of the Cultivated Mushroom," ed. P.B. Flegg, D.M. Spencer, and D.A. Wood, p. 195-210. John Wiley & Sons Ltd., New York.
- Nisperos-Carriedo, M.O., Baldwin, E.A., and Shaw, P.E. 1991. Development of an edible coating for extending postharvest life of selected fruits and vegetables. *Proc. Florida State Hort. Soc.*, No. 104, pp. 122-125.
- Norman, S.I. 1990. Juice enhancement by ion exchange and adsorbent technologies. In "Production and Packaging of Non-Carbonated Fruit Juices and Fruit Beverages," ed. D. Hicks, pp. 243-263. Blackie-Van Nostrand Reinhold, New York.
- O'Brien, J. and Morrissey, P.A. 1989. Nutritional and toxicological aspects of the Maillard browning reaction in foods. *Crit. Rev. Food Sci. Nutr.* 28: 211-248.
- Oszmianski, J. and Lee, C.Y. 1990. Inhibition of polyphenol oxidase activity and browning by honey. *J. Agric. Food Chem.* 38: 1892-1895.
- Ponting, J.D., and Jackson, R. 1972. Prefreezing processing of Golden Delicious apple slices. *J. Food Sci.* 37: 812-814.
- Santerre, C.R., Cash, J.N., and Vannorman, D.J. 1988. Ascorbic acid/citric acid combinations in the processing of frozen apple slices. *J. Food Sci.* 53: 1713-1716, 1736.
- Santerre, C.R., Leach, T.F., and Cash, J.N. 1991. Bisulfite alternatives in processing abrasion-peeled Russet Burbank potatoes. *J. Food Sci.* 56: 257-259.
- Sapers, G.M. 1986. Unpublished data. Eastern Regional Research Center, U.S. Dept. of Agriculture, Philadelphia, Pa.
- Sapers, G.M. and Douglas, F.W. Jr. 1987. Measurement of enzymatic browning at cut surfaces and in juice of raw apple and pear fruits. *J. Food Sci.* 52: 1258-1262, 1285.
- Sapers, G.M. and Hicks, K.B. 1989. Inhibition of enzymatic browning in fruits and vegetables. In "Quality Factors of Fruits and Vegetables: Chemistry and Technology," ed. J.J. Jen, ACS Symp. Series 405, pp. 29-43. Am. Chem. Soc., Washington, D.C.
- Sapers, G.M. and Miller, R.L. 1992. Enzymatic browning control in potato with ascorbic acid-2-phosphates. *J. Food Sci.* 57: 1132-1135.
- Sapers, G.M., Douglas, F.W. Jr., Bilyk, A., Hsu, A.-F., Dower, H.W., Garzarella, L., and Kozempel, M. 1989a. Enzymatic browning in Atlantic potatoes and related cultivars. *J. Food Sci.* 54: 362-365.
- Sapers, G.M., Hicks, K.B., Phillips, J.G., Garzarella, L.G., Pondish, D.L., Matulaitis, R.M., McCormack, T.J., Sondey, S.M., Seib, P.A., and El-Atawy, Y.S. 1989b. Control of enzymatic browning in apple with ascorbic acid derivatives, polyphenol oxidase inhibitors, and complexing agents. *J. Food Sci.* 54: 997-1002, 1012.
- Sapers, G.M., Garzarella, L., and Pilizota, V. 1990. Application of browning inhibitors to cut apple and potato by vacuum and pressure infiltration. *J. Food Sci.* 55: 1049-1053.
- Sayavedra-Soto, L.A. and Montgomery, M.W. 1986. Inhibition of polyphenoloxidase by sulfite. *J. Food Sci.* 51: 1531-1536.
- Shewfelt, R.L. 1986. Flavor and color of fruits as affected by processing. In "Commercial Fruit Processing," 2nd ed., ed. J.G. Woodroof and B.S. Luh, pp. 481-529. AVI Pub. Co. Westport, Conn.
- Sims, C.A., Johnson, R.P., and Bates, R.P. 1989. Quality of a non-sulfited *Vitis rotundifolia* and a *Euvitis* hybrid white wine produced from ultrafiltered juice. *Am. J. Enol. Viticulture* 40: 272-276.
- Smith, O. 1987a. Effect of cultural and environmental conditions on potatoes for processing. In "Potato Processing, 4th ed," ed. W.F. Talburt and O. Smith, pp. 73-147. AVI-Van Nostrand Reinhold, New York.
- Smith, O. 1987b. Transport and storage of potatoes. In "Potato Processing," 4th ed., ed. W.F. Talburt and O. Smith, pp. 203-285. AVI-Van Nostrand Reinhold, New York.
- Tamminga, S.K., Beumer, R.R., Keijbets, M.J.H., and Kampelmacher, E.H. 1978. Microbial spoilage and development of food poisoning bacteria in peeled, completely or partly cooked vacuum packed potato. *Archiv für Lebensmittelhygiene* 29: 215-219.
- Taoukis, P.S., Labuza, T.P., Lillemo, J.H., and Lin, S.W. 1990. Inhibition of shrimp melanosis (black spot) by ficin. *Lebensm. Wiss. Technol.* 23: 52-54.
- Taylor, S.L., Higley, N.A., and Bush, R.K. 1986. Sulfites in foods: Uses, analytical methods, residues, fate, exposure assessment, metabolism, toxicity, and hypersensitivity. *Adv. Food Res.* 30: 1-76.
- Tong, C.B.S. and Hicks, K.B. 1991. Sulfated polysaccharides inhibit browning of apple juice and diced apples. *J. Agric. Food Chem.* 39: 1719-1722.
- Tressler, D.K. and DuBois, C. 1944. No browning of cut fruit when treated by new process. *Food Ind.* 16(9): 701, 763-765.
- Vamos-Vigyazo, L. 1981. Polyphenol oxidase and peroxidase in fruits and vegetables. *CRC Crit. Rev. Food Sci. Nutr.* 15: 49-127.
- Van Buren, J.P. 1989. Causes and prevention of turbidity in apple juice. In "Processed Apple Products," ed. D.D. Downing, pp. 97-120. AVI-Van Nostrand Reinhold, New York.
- Walker, J.R.L. 1976. The control of enzymatic browning in fruit juices by cinnamic acids. *J. Food Technol.* 11: 341-345.
- Waller, G.R. and Feather, M.S. 1983. The Maillard Reaction in Foods and Nutrition." ACS Symp. Series 215. Am. Chem. Soc., Washington, D.C.
- Warren, B.Z. 1991. Food preservative compositions. U.S. patent 4,988,522.
- Wedzicha, B.L. 1987. Review: Chemistry of sulphur dioxide in vegetable dehydration. *Intl. J. Food Sci. Technol.* 22: 433-450.
- Wedzicha, B.L. and Goddard, S.J. 1988. The dissociation constant of hydrogen sulphite ion at high ionic strength. *Food Chem.* 30: 67-71.
- Wei, C.I., Fernando, S.Y., and Huang, T.S. 1990. Mutagenicity studies of kojic acid. *Proc. 15th Annual Conf., Tropical and Subtropical Fisheries Technology Conf. of*