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REVIEW

Approaches to the Citrus Browning Problem. A Review

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When subjected to nonrefrigerated storage, citrus juices rapidly develop objectionable flavor and color. Sugar breakdown through the Maillard reaction is initiated by formation of hexose amines from amino acids and sugars present in citrus juice and proceeds through the Amadori (or Heyns) rearrangement to produce deoxy amino hexoses. These deoxy compounds go through a series of dehydrations, deaminations, and enolizations to produce either 1-deoxy-2,3-dicarbonyls or 3-deoxy-1,2-dicarbonyls. The pathway depends upon a relationship between the pH of the juice and the basicity of the amine. The 1-deoxy compounds further react to produce furanones and pyrones, whereas the 3-deoxy compounds produce furfurals and pyrroles. Both pathways are known to be operable because all four types of compounds are found in citrus juice and some of these have been shown to have taste significance. Ascorbic and dehydroascorbic acids may enter into the browning scheme as highly reactive α -dicarbonyls similar to those derived from the sugars.

Browning of citrus products has been a problem throughout the history of the processing industry. Maintaining the product at low temperature has been and still is (*Citrus World*, 1984) the only means to avoid color and flavor deterioration of processed citrus fruit juices, concentrates, and dehydrated products in long-term storage (Van Loesecke et al., 1934; Loeffler, 1941; Curl, 1947). Although color changes are still a concern in citrus products (Karakasides and Marousakis, 1981; *Citrus World*, 1984), the series of reactions culminating in formation of brown pigment are preceded or accompanied by other reactions that produce smaller molecules having taste significance. Thus, flavor usually becomes unacceptable before there is an objectionable color change (Shaw et al., 1977).

For 50 years compositional changes that relate to taste change have been the subject of studies with orange juice and juice simulation models. From this review of these studies it is concluded that adverse flavor changes associated with browning result from formation of compounds that impart objectionable flavor at low concentrations.

ROLE OF AMINO ACIDS

The early work of Curl (1949), Joslyn (1957), Wolfrom (1974), and others showed that amino acids accelerate sugar breakdown to produce brown color, and the model studies of Jurch and Tatum (1970) and Shaw and Berry (1977) show that amine catalysis produced compounds of taste significance. Specifically, Huffman (1974) and Varsel

(1980) made direct claims that naturally occurring amino acids cause or accelerate flavor damage in orange juice. It is also noteworthy that a great number of studies with products other than citrus and models have demonstrated that amine-assisted sugar breakdown is the source of most cooked, baked, or otherwise heated food aromas (Reynolds, 1970; Fors, 1983). It should be noted, however, that there is a great similarity between acid-catalyzed and amine-catalyzed degradation of sugars. The major difference is that milder conditions of heat and acidity are needed in the latter case.

Isotope exchange experiments (Hicks and Feather, 1975) show that the same compounds, such as the deoxy sugars, the dicarbonyls, and their enols, and other browning intermediates are formed in either case. The basis for the milder conditions is that the Amadori compounds apparently enolize and convert to reactive browning intermediates much faster, because of the amine substituent in the sugar molecule (Feather, 1982). In models simulating orange juice, many end products of browning are found both in the presence and in the absence of amines (Shaw et al., 1977). However, quantitative data are not available so we have no estimate of the extent to which amines cause or enhance sugar breakdown and formation of compounds of taste significance.

Although there is still very little known about the brown polymers produced in nonenzymic browning, it is interesting to note that a recent study of polymers produced from the interaction of glycine with D-glucose, D-fructose, and (hydroxymethyl)furfural were similar and suggest that the amino acid is incorporated into the material. This interaction was confirmed by elemental analyses. Calculations for the polymers derived from D-glucose and D-

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Table I. Compounds Isolated from Orange Juice and Model Studies

compound isolated	model studies ^a								
	orange juice		fructose				rham-Ala (pH 3.5)	gluco-Meam	asc acid
	dehydr	canned	acid (pH 3.5)	base (pH 8.0)	ala (pH 3.5)	γ -abu (pH 3.5)			
furfuryl alcohol	x		x	x	x		x		
5-methylfurfural	x		x		x		x		
furfural	x	x	x	x	x			x	
5-(hydroxymethyl)furfural	x	x	x	x	x		x	x	
2-(hydroxyacetyl)furan	x	x	x		x			x	
2-acetylfuran	x				x			x	
2-acetylpyrrole	x				x				
5-methylpyrrole-2-carboxaldehyde	x				x				
<i>N</i> -ethylpyrrole-2-carboxaldehyde ^b	x						<i>N</i> -Me		
acetic acid	x		x	x		x	tr	x	
levulinic acid	x		x						
benzoic acid	x	x		x					
tiglic acid	x								
2,5-dimethyl-4-hydroxy-3(2 <i>H</i>)-furanone ^b		x		x			x	x	
3-hydroxy-2-pyrone	x	x						x	
2,3-dihydro-3,5-hydroxy-6-methyl-4 <i>H</i> -pyranone	x		x	x			x		
acetylformoin	x		x				x		
hydroxymethylcyclopenteneone ^b	x			x	x		x	x	
γ -butyrolactone	x			x					
α -terpineol ^b		x (possibly derived from <i>d</i> -limonene)							
4-vinylguaiaicol ^b		x (possibly derived from decarboxylation of ferulic acid)							

^a Abbreviations: Ala, alanine; γ -abu, aminobutyric acid, rham, rhamnose; gluco, glucose; Meam, methylamine; asc, ascorbic. ^b Probably of taste significance.

fructose with glycine suggested that the polymer is composed of sugar and amino acid residue minus 3 mol of water (Feather and Nelson, 1984).

Of the specific components of citrus juices that react in Maillard browning, the amino acids have the most prominent and diverse set of roles. That the amino acids are involved in nonenzymic browning of citrus was established in experiments where their removal by ion-exchange resins increased stability against deteriorative change. Onayemi and Bruemmer (1984) stabilized color of grapefruit syrups by removal of cations. Earlier, Bruemmer and Bowers (1977) found that the color of orange syrup was similarly stabilized. Clegg (1969) showed that darkening of lemon juice was delayed by removal of amino nitrogen by cation exchange. In 1974 Huffman obtained a patent, claiming increased flavor stability, by treating orange concentrate with cation-exchange resin. Earlier (1957) Joselyn reported that anion and cation removal by ion exchange were both beneficial in delaying development of brown color. Numerous model studies, simulating citrus juice composition, confirm that amino acids cause an acceleration of browning, (Curl, 1949; Clegg, 1964; Joselyn, 1957). It is further concluded (Wolfrom et al., 1974) that amino acids engage in the degradation reactions of the sugars, γ -aminobutyric acid being the most reactive followed closely by arginine.

Off-flavor development in dehydrated orange juice is attended by production of at least 18 compounds not present in the fresh products (Tatum et al., 1967; Shaw et al., 1970) (Table I). Of these, only three were found at levels approaching their taste thresholds (Shaw et al., 1970). These three, *N*-ethylpyrrole-2-carboxaldehyde, hydroxymethylcyclopentenone, and 5-methyl-2-furaldehyde were found to have a synergetic effect when combined, at half of each one's threshold level. The taste response was typical of aged or heat-abused dehydrated orange juice.

The mechanism for the reaction producing pyrroles was studied by Shaw and Berry (1977) using fructose- γ -aminobutyric acid, fructose-alanine, rhamnose-alanine, and fructose-hydrochloric acid (at pH 3.5). In those studies the rate of brown color formation and furan production was much faster in the presence of amino acids.

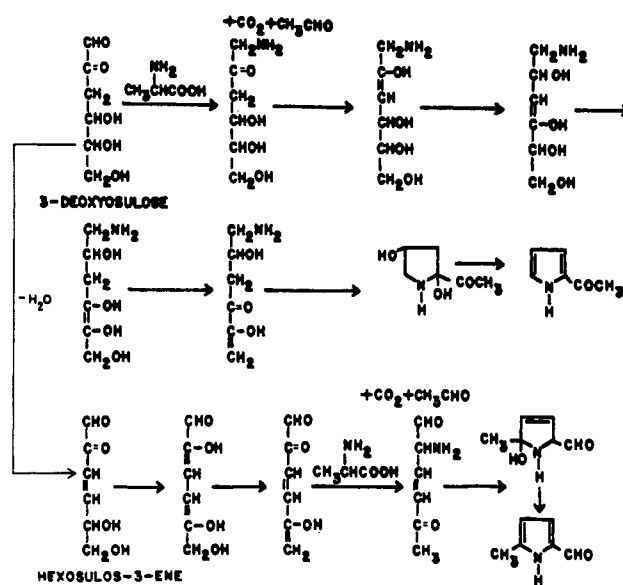


Figure 1. Synthesis of the two pyrroles by Strecker degradation.

Both sugars produced 2-furaldehydes, rhamnose, 5-methyl-2-furaldehyde, and fructose, 5-(hydroxymethyl)-2-furaldehyde. The rhamnose-alanine mixture produced no pyrrole from the expected reaction of alanine with 3-deoxy hexosuloses (known to be present because furans were produced) (Kato and Fujimaki, 1968; Kato, 1967). Two pyrroles, 2-acetylpyrrole and 5-methylpyrrole-2-carboxaldehyde, were however produced in the fructose-alanine reaction. The mechanism proposed for these reactions involves Strecker degradations in which the α -dicarbonyl, 3-deoxy hexosulose derivative of fructose reacts with α -alanine to produce a 1-amino-3-deoxy 2-ketose as depicted in Figure 1. The sugar derivative undergoes reduction; thus, 2-acetylpyrrole is formed after a series of enolization and dehydration steps. On the other hand, the 3-deoxy hexosulose can dehydrate to the hexosulos-3-ene and then undergo enolization, obtain an amino group through Strecker degradation of alanine, and undergo ring closure and dehydration to give 5-methylpyrrole-2-

Table II. Taste Significance of Compounds

compound	taste thresh- old ^a	concn ^a found	odor	source ^b
4-vinylguaiaicol ^c	0.05	1	bad	c
2,5-dimethyl-4-hydroxy-3(2H)-furanone	0.05	?	pineapple	c
α -terpineol ^c	2	4	piney-stale	c
<i>N</i> -ethylpyrrole-2-carboxaldehyde	2	0.5		d
hydroxymethyl-cyclopentenone	5	1	maple syrup	d
5-methylfurfural	10	<.5		d
acetylformoin	18	<.5		d
3-hydroxy-2-pyrone	30	1		c, d
furfuryl alcohol	30	<.5		d
furfural	80			c, d
5-(hydroxymethyl)-furfural	>200	14		c, d

^aIn ppm. ^bSource: c = canned; d = dehydrated. ^cNot a sugar-breakdown product.

carboxaldehyde. These two pyrroles were identified as storage decomposition products in dehydrated orange juice along with the highly flavorful 5-methyl-2-furaldehyde and *N*-ethylpyrrole-2-carboxaldehyde. The *N*-ethyl compound was not found in these studies. However, Jurch and Tatum isolated *N*-methylpyrrole-2-carboxaldehyde from a reaction of glucose with methylamine. Subsequent studies of pyrrole formation mechanisms (Nyhammer et al., 1983) using [1-¹³C]-D-glucose and glycine confirmed the mechanisms shown for glucose, although the authors speculated whether or not a Heyns rearrangement of fructose would give rise to the necessary intermediate for 2-acetylpyrrole production from fructose.

Strecker degradations of amino acids result in Strecker aldehydes, which are sometimes contributors of off-flavor. For example, isovaleraldehyde derived from leucine contributes an off-flavor in dehydrated carrots (Eichner and Wolf, 1983). Strecker aldehydes have not been reported as contributors to off-flavor in dehydrated orange juice, however.

Hydroxymethylcyclopentenone (having a maple-like flavor), one of the major contributors to the heat-abused flavor, typical of aged dehydrated orange juice (Shaw et al., 1970), was produced from rhamnose and from fructose in acid solutions with alanine (Shaw and Berry, 1977). This compound probably resulted from amine-assisted sugar dehydration, although other studies showed it may be a product of breakdown of ascorbic acid (Tatum et al., 1969).

Five of the compounds found in dehydrated orange juice (Table I) are also found in canned single-strength orange juice. In this product, three different compounds were found to have taste significance when combined each at half its threshold level. These were α -terpineol, 4-vinylguaiaicol, and 2,5-dimethyl-4-hydroxy-3(2H)-furanone (Table II). The α -terpineol and 4-vinylguaiaicol are not sugar breakdown products; α -terpineol probably derives from *d*-limonene and 4-vinylguaiaicol from ferulic acid.

The compound 2,5-dimethyl-4-hydroxy-3(2H)-furanone, with a pineapple-like flavor (Rodin et al., 1965), isolated from aged canned orange juice (Tatum et al., 1975) was identified by Shaw et al. (1971). This compound was produced in appreciable quantities in the reaction of rhamnose with alanine in acid solution (Shaw and Berry, 1977). The mechanism of the reaction is probably the classic 2,3-enolization pathway from the Amadori compound. The 1,2-enolization pathway was also operable in this study because a major amount of 5-methyl-2-fur-

aldehyde was produced. The 5-methyl isomer resulted because rhamnose is a 6-deoxy hexose.

ROLE OF THE SUGARS

Whether the undesirable flavors that develop in citrus products result from breakdown of specific carbohydrates or from all that are present is not known. Citrus juices contain mainly sucrose, fructose, and glucose, but a number of other sugars are present in small amounts. The many differences in the ways that fructose and glucose react lie in the position of the reactive carbonyl. Glucose reacts with amino acids and then rearranges to produce 1-amino-1-deoxyfructose (ADF) while fructose yields 2-amino-2-deoxyglucose (ADG). According to Van den Ouweland et al. (1978), ADG undergoes only the 1,2-enolization to produce 1,2-dicarbonyl-3-deoxy osulose. The finding of pyrones, believed to be formed only by 2,3-enolization, on thermal degradation of a dry melt of a fructose and glycine reaction product, is explained by these authors by assuming that a condensation reaction occurred between the carbohydrate chain scission products methylglyoxal and dihydroxyacetone. These authors also point out that in fructose degradation with glycine more carbohydrate chain scission products are formed and nitrogen seems to play a more active role than it does in glucose degradation with glycine; i.e., more amines, pyrroles, and pyrazines are formed. On the other hand, Feather (1982) reports that in acid-catalyzed breakdown of both glucose and fructose a 1,2-enediol is an intermediate and therefore, depending on pH, either the 1,2- or the 2,3-enolization route would be followed. In aqueous model solutions simulating the pH of citrus juices, glucose breakdown catalyzed methylamine in acetic acid produced a furanone and a pyranone (Jurch and Tatum, 1970). On the other hand, fructose breakdown catalyzed by alanine or γ -aminobutyric acid at pH 3.5 produced neither compound (Shaw and Berry, 1977). These findings indicate that 2,3-enolization takes place with glucose but not with fructose in dilute aqueous solutions at low pH.

Other sugars are present in orange juice at concentrations high enough to be precursors for the trace amounts of flavor compounds necessary to render a product objectionable. Some of these have been used in model studies. Sugars behave similarly when subjected to conditions that favor browning as demonstrated in numerous studies (Feather, 1982 and references therein). Nevertheless, there are some differences worthy of note. Rhamnose reacted with alanine at pH 3.5 to produce the highly flavorful 2,5-dimethyl-4-hydroxy-3(2H)-furanone (Shaw and Berry, 1977). Doornbos and Van den Ouweland (1981) demonstrated this with other amino acids and other 6-deoxy aldose sugars. Under the same conditions fructose did not yield a furanone. Instead, two furans and two pyrroles were formed (Shaw and Berry, 1977). The reason for this may be that, in the case of hexoses, the products arising from 2,3-enolization, maltol and isomaltol, are not stable in aqueous medium and, if formed, disappeared rapidly (Feather, 1982). Rhamnose is a minor constituent of citrus pectin while galacturonic acid is the main constituent (Nagy et al., 1977). Rhamnose and galacturonic acid become constituents of citrus juices when enzymic degradation of pectin occurs in juice processing. The uronic acids undergo acid-catalyzed degradation (Seaver and Kertez, 1946; Feather, 1982) to produce 2-furaldehyde and reductic acid (2,3-dihydrocyclopenten-1-one). The hexuronic acids decarboxylate to produce 5-carbon end products. They also break down without decarboxylation to produce small quantities of 5-formyl-2-furoic acid. The uronic acids, like the sugars, break down under less severe

conditions and brown more rapidly when catalyzed by amines than under acid catalysis. The isolation of 4-hydroxy-5-methyl-3(2*H*)-furanone (a component of beef flavor and aroma and a homologue of the pineapple flavor furanone) from heating an Amadori compound of D-fructuronic acid (1-deoxy-1-(dibenzylamino)-D-fructuronic acid) at pH 6 illustrates the 2,3-enolization pathway at the higher pH. Severin and Seilmeier (1967) were the first to isolate this compound. They reacted pentoses with the acetates of primary amines. At the higher acidity (2 N H₂SO₄) with heating, the Amadori compound produced 2-furaldehyde and reductic acid. Nursten (1980), in a review of food flavor development, pointed out that the 2,3-enolization pathway is not only the source of the highly flavorful furanone 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone and the 5-methyl homologue mentioned above, but also the pyrones such as maltol, which are highly important flavors in baked products. A pyrone (2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyranone) was also isolated from dehydrated orange juice (Shaw et al., 1967), from acid-catalyzed fructose degradation (Shaw et al., 1967) and from a D-glucose, methylamine, and acetic acid degradation reaction (Jurch and Tatum, 1970). This pyrone undergoes acid-catalyzed rearrangement to give isomaltol, a furan derivative, while dehydration affords maltol (Shaw et al., 1971). It was also demonstrated (Mills, 1978) that this compound underwent ring contractions to produce the important pineapple-like furanone (Rodin, 1965) and a nearly odorless hydroxymethyl derivative, 2-methyl-4-hydroxy-5-(hydroxymethyl)-3(2*H*)-furanone.

Perhaps the enhanced rates of reaction and the different reaction end products encountered in lowered water activity products are the result of dehydrating conditions favoring pyranone formation. On the other hand, furanone formation from hexoses occurs under conditions favoring allylic hydroxy elimination to deoxygenate the sixth carbon so a 5-membered furanone ring forms (Mills et al., 1969). This is what happens in the case of orange juice: the pyranone is found in the dehydrated product, and the furanone occurs in canned juice (Table I). The model study (Shaw and Berry, 1977) shows that rhamnose may be the carbohydrate source. The furanone has a taste threshold of 0.05 ppm, and the pyranone has a taste threshold greater than 200 ppm. This 4000-fold difference accounts for the fact that the furanone imparts an undesirable taste. Unfortunately, studies of the reaction kinetics have emphasized the more easily measured changes in color and other empirical indices and have developed very little data on those reactions producing compounds of taste significance. Notable exceptions are Eichner and Cinar-Doruk (1981) and Eichner and Wolf (1982) who developed quantitative data on the generation of Amadori compounds, Strecker aldehydes, and other indices relating to taste change in dehydrated vegetables.

ROLE OF ASCORBIC ACID

Ascorbic acid degradation has been associated with browning of orange juice since before 1935 (Joslyn and Marsh, 1935; Varsel, 1980 and references therein); it has been demonstrated that amino acids accelerate ascorbic acid breakdown (Joslyn, 1957; Clegg, 1964; Seck and Crouzet, 1981), and in the presence of amine it is dehydroascorbic acid that is the reactive intermediate (Hodge, 1953; Joslyn, 1957; Clegg, 1964) in the pathway to furfural and brown pigment production. Kurata and Sakurai (1967) and Tatum et al. (1969) showed that when ascorbic acid breaks down by acid catalysis, furfural is also the main end product, but according to Kurata and Sakurai (1967), no intermediate oxidation to dehydroascorbic acid occurs.

These authors also concluded that acid catalysis is functional even under oxidative conditions and that ascorbic acid is partially responsible for orange juice discoloration.

Since it was observed that ascorbic acid breakdown in orange juice results in furfural production and furfural buildup closely parallels quality loss in citrus products, furfural indexing has been proposed as a basis for quality control (Dinsmore and Nagy, 1972; Nagy et al., 1972; Nagy and Randall, 1973; Nagy and Dinsmore, 1974; Herrmann and Partassidou, 1979). It is not that furfural, per se, contributes appreciably to off-flavor; the levels present are below the taste detection threshold (Nagy and Dinsmore, 1974). In addition to ascorbic acid, the pentoses and uronic acids are also known to produce furfural on breakdown.

ROLE OF BUFFER AND CATALYSTS

That color formation is enhanced by the citrate ion has been demonstrated by several workers (Clegg, 1966; Wolfrom et al., 1974; Reyes and Toledo, 1982), although no specific role was proposed. A discussion of the effects of pH and buffers by Spark (1969) indicates that buffering results in an increased browning rate. This is supported by Heyns and Reinhold (1981) who found the rate of formation of amino sugars progresses linearly with the log of the buffer concentration. In the absence of buffers, the pH drop is rapid when aldose sugars combine with an amine to form the aldosylamine, the pH drop being the result of removing the basic amino group of the amine. The rate-controlling factor in this reaction is mainly the mutarotation rate of the sugar, which in turn is dependent on pH. Heyns and Rheinhold (1981) report that the reaction rate correlates with the open-chain keto form content of fructose and not with the cyclic form. However, Westphal et al. (1984) and Westphal and Cieslik (1981) report that, in the first step of the Maillard reaction, glucose exists preferably with the OH group in the equatorial configuration of the β -pyranose anomer. According to Spark (1969), buffering a sugar and amino acid system will be expected to accelerate the formation of ketosylamine or aldosylamine. The fact that the Amadori and Heyns rearrangements are acid and base catalyzed suggests that these also would be accelerated by buffers. Spark (1969) also points out that phosphate accelerates initial browning regardless of any buffering effect. Hodge and Fisher (1963) reported that although proton donors were necessary to bring about the Amadori rearrangement of aldosylamines to 1-amino-1-deoxy ketoses or the Heyns rearrangement of ketosylamines to 2-amino-2-deoxy aldoses, the amino acids supply the necessary protons when they are condensed with sugar and no other acid need be added. It was reported (Hodge and Rist, 1953) that compounds with active methylene groups (e.g., malonic acid or diphenylmethane) were effective in promoting the rearrangement. They speculated that the active methylene group engaged in a temporary condensation (Knoevenagel type) with the ketose derivative. They point out that the active hydrogen would also allow formation of the quaternary base cations thought to be intermediates in the rearrangement. It is interesting to note that, in later work, Mills and Hodge (1976) used malonic acid to catalyze synthesis of 1-deoxy-1-L-proline-D-fructose. The finding that citric acid enhances color formation in model systems simulating citrus juices may be explainable on the basis that citric acid acts as a buffer across a broad pH range. It also has active methylene groups that promote the Amadori rearrangement.

SULFUR DIOXIDE

No discussion of attempts to control deteriorative browning should omit mention of bisulfite and the effects

of this preservative upon the progress of the browning reaction. From a practical standpoint, addition of bisulfite will extend shelf life of citrus products (Shaw et al., 1970). McWeeny's (1981) review concluded that there are still considerable gaps in knowledge concerning the ways in which sulfur dioxide controls the Maillard reaction in foods. But we know that it does affect the early stages of the reactions, combines with active intermediates, and bleaches the final color. According to Wedzicha and Imeson (1977) it forms stable sulfonates of the α,β -unsaturated dicarbonyls. For example, 3-deoxy pentosulose, a breakdown product of ascorbic acid, reacts with SO_2 to form a stable dihydroxy sulfonate of 3-deoxy-4-sulfo pentosulose a 1,2,4-trisulfonate stabilized by hydrogen bonding. This structure was first proposed for the hexosuloses by Knowles (1971). Wedzicha (1984) studied kinetic data and concluded that the monohydroxy sulfonate is probably the predominant structure.

ROLE OF SULFUR-CONTAINING AMINO ACIDS AND THIOLS

Reactions of the sulfur-containing amino acids (cysteine, cysteine, methionine) with sugars and other carbonyl-containing compounds in foods result in formation of thiophenes, mercaptofurans, thiazolines, thiazoles, heterocyclic polysulfides, and other sulfur-containing heterocycles (Shu et al., 1985; Sakaguchi and Shibamoto, 1978; Arroyo and Lillard, 1970; Scalan et al., 1973). The Strecker degradation is a major source of intermediates for these compounds (Bailey, 1983). These compounds along with the hydrazines are extremely important in the flavors developed in cooked meat (Bailey, 1983), cereal products, and certain vegetables (Fors, 1983), although none are reported in browned fruit products.

Aside from these reactions, which produce compounds of taste significance, the sulfur-containing amino acids and thiols are known to inhibit browning. Cysteine inhibits browning of pear juice concentrate (Montgomery, 1983) and prevents flavor change. Lightbody and Fevold (1948) found that the addition of cysteine to dried egg products prevented browning and insolubility. Reynolds (1965) reported that browning from the reaction of glucose and glycine (but not furfural and glycine) was inhibited by thiols such as 2-mercaptoethanol or mercaptoacetic acids. Mercaptoacetic and 3-mercaptopropionic acids inhibited browning while acting as catalysts for the Amadori rearrangement of glucose with secondary amine reaction products (Hodge, 1955; Hodge and Fisher, 1963). Thiophenol and several other mercaptans catalyzed the Amadori rearrangement of D-glucosylmorpholine to 1-deoxy-1-morpholino-D-fructose in 85% yield with negligible browning (Ingles, 1963).

CONCLUSIONS

Reducing sugars, ascorbic acid, and probably other carbonyl compounds present in citrus fruit are the suspected reactants in browning phenomena and the precursors to compounds of taste significance. Amines and amino acids present catalyze the initial reactions and also take part in later sequences of reactions that occur. Some compounds of taste significance have been identified and mechanisms for their formation proposed. Better and more practical means need to be developed to control the interactions of various compositional factors to reduce deleterious changes.

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