Control of Enzymatic Browning in Green Bananas for Freezing[1]

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ABSTRACT

When green bananas are peeled by heating in steam at 80 lb pressure for 30 s the polyphenol oxidase is inactivated in a heat ring to a depth of ⅛ in (3.1 mm), but not in the interior pulp of the fruit. Increasing the length of the peeling treatment, alone or in combination with hot water or steam blanching, could not be used to inactivate the enzyme system due to the excessive softening of the pulp. Dipping the steamed fruit in citric acid solutions 1 to 5% w/w reduced browning in the exposed surfaces only. When slices 1½ in thick were sulfited to 412 p/m SO_2, a high SO_2 content was reached in the heat ring but the core had a resultant sulfite content of 22–32 p/m. The polyphenol oxidase in an area around the degenerated ovules and immature seeds was not inactivated. When the whole fruit was sulfited, no sulfite reached the inner tissue. Sulfiting by dipping in $K_2S_2O_5$ solutions for 240 min at an SO_2 level of 1,289 p/m failed to inactivate the polyphenol oxidase in the interior tissue. During thawing, diffusion of sulfite to the inner tissue was slow, and even after thawing for 6 h, complete inactivation of the polyphenol oxidase was not achieved. Sulfited bananas with the enzyme system active in the interior pulp showed browning when thawed and exposed to the air. Complete enzyme inactivation and absolute control of the browning reaction was achieved by heating the raw fruit in water at 200° F (93° C) for 30 min. Besides controlling browning, the hot water treatment loosens the peel, facilitating its subsequent removal by hand.

INTRODUCTION

When freezing green bananas, it is important to control enzymatic browning which takes place when tissue with an active oxidative enzyme system is exposed to air. Development of dark pigments greatly affects both appearance and quality of the frozen product. Griffith (3) showed that the browning reaction of bananas resulted from enzyme oxidation of dopamine by a polyphenol oxidase. Palmer (5) confirmed that the phenol oxidase in bananas is polyphenol oxidase, with dopamine being the most readily oxidized substrate. Montgomery and Sgarbieri (4) showed the presence of nine polyphenol oxidase isoenzymes in the interior of the banana pulp, eight in the exterior and ten in the peel. Polyphenol oxidase activity was found to be most concentrated in the interior of the fruit, in the tissue adjacent to the degenerated ovules and immature seeds. Some of the isoenzymes of the pulp were found to be uninhibited by sodium metabisulfite.

In the processing of fruit and vegetables, polyphenol oxidase may be

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inactivated by three methods: heat, sulfitation, and lowering of the pH to reduce enzyme activity (7). Effectiveness of the method in controlling browning in the particular product processed, without adversely affecting flavor and quality, determines the method selected.

This paper reports results of studies conducted to determine the most adequate procedure to control browning reaction in green bananas for freezing.

MATERIALS AND METHODS

Bananas used in this study were purchased from a ripening plant the same day they were received at the plant. The stage of development ranged from light three-quarters to full. Postharvest handling and storage before delivery to the ripening plant was not known. The bananas processed were of the Montecristo cultivar, which is generally grown in Puerto Rico.

The green fruit was stored at 45° F (7.2° C) until processed. Two methods were used for peeling the fruit: 1) Hot-water peeling: The hands were cut off from the main stem and submerged in water at 200° F (93° C) for 30 min. After the hot-water treatment, the fruit was cooled in water until the temperature dropped enough for handling. The peel was removed by hand and the peeled fruit was kept under water at room temperature until further processed; 2) Steam peeling: The fruit was treated in a retort at 80 lb/in^{2}g for 30 s. On discharge from the retort the fruit was peeled and handled as described for the hot-water-treated fruit.

The peeled fruit was sliced into quarters by hand or by a homemade slicer. The fruit was sulfited by dipping in $K_2S_2O_5$ solutions at room temperature, concentration of the sulfiting solution being adjusted as required by the experiment. Citric acid was added to adjust the pH of the sulfiting solution to the desired value.

To determine the time:temperature relationship for enzyme inactivation, copper-constantan thermocouples were inserted in the center of the fruit and the temperature read from a calibrated potentiometer. Phenolase activity was determined by placing in an open petri dish a thin slice cut across the fruit and bathing it with a 1% cathecol solution. Positive enzyme activity was indicated by the development of a brown color in the tissue within 5 min of exposure to air (6). The diameter of the area showing a positive reaction to cathecol was recorded.

For blanching studies three methods were used. For water blanching, the fruit was placed in a tank of water with temperature controlled by means of a pneumatic indicating temperature controller. For steam blanching, the fruit was placed on the wire mesh conveyor of a drapper blancher, exposed to steam for the desired time, and subsequently cooled to room temperature with water sprays. In other experiments, the fruit

was blanched in a screw-type thermotic blancher and cooled by dipping in water at room temperature.

The SO_2 content of the sulfiting solution was determined by the method described in the Food Chemical Codex (2). The SO_2 content in raw and frozen slices was determined by the method of Ross and Treadway (8). Sulfite content is expressed as p/m SO_2.

RESULTS AND DISCUSSION

STEAM-PEELED FRUIT

Enzyme Heat Inactivation

When green bananas are steamed at 80 lb/in^{2}g for 30 s to facilitate peel removal, the enzyme polyphenol oxidase is inactivated in a heat ring of about ⅛ in (3 mm) depth, but not in the inner tissue. When the steam-treated fruit is sliced or trimmed, the surface exposed below the heat ring rapidly develops an intense browning. The browning reaction is most intense in the tissue around the ovules and immature seeds. To freeze a product of good quality, the browning reaction must be controlled immediately after peeling.

Since steam peeling involves heat treatment of the fruit, investigation was made of the possibility of inactivating the polyphenol oxidase by prolonging the steaming operation or by combining a blanching treatment with the peeling treatment.

Heat inactivation of the enzyme system during the steaming operation at 80 lb steam pressure proved to be impractical. The time required to inactivate the enzyme system in the whole fruit cooked the fruit to such an extent that it was unsuitable for freezing. Reducing steam pressure and extending heating time was not feasible either. When bananas were heated at 15 lb steam pressure for 15 min peel removal was not satisfactory and the inner pulp showed a positive cathecol test, indicating the presence of active polyphenol oxidase.

The results of tests in which the time:temperature relationship for inactivating the polyphenol oxidase in green bananas was determined showed that to achieve complete enzyme inactivation the inner tissue of fruit must be heated to a temperature of 197° F (91.5° C). When steam-treated unpeeled fruit, either whole or sliced, with an initial center temperature of 120–133° F (49–55° C) was heated in water at 200° F (93° C), the polyphenol oxidase was inactivated in 10 to 12 min. Increasing the water temperature to 210° F (99° C) reduced the time needed to inactivate the enzyme system by only one minute.

Although the enzyme system in the steam-peeled fruit could be inactivated by blanching in water at 200° F (93° C) for 12 min, this treatment proved to be undesirable. Blanching for such a long time cooked and

softened the surface layer of pulp to the extent that it was washed away quite easily by the water sprays in the cooling operation. As a result of the loss of the upper layer of pulp, the blanched fruit looked rough and unattractive.

Steam blanching of the steam-peeled fruit was attempted using a drapper type blancher and a thermotic screw type blancher. In both cases the fruit was excessively cooked and softened in the time required to inactivate the polyphenol oxidase, which exceeded 10 min. Loss of pulp during blanching and cooling was high and the appearance of the steam-blanched fruit was also very poor.

Acid Treatments

Table 1 shows the effect of a citric acid dip on the browning of steam-peeled bananas. When the concentration of citric acid was increased from 1 to 5%, the percentage of browning on the surface decreased. Although dipping the peeled fruit for 5 min in citric acid solutions of 3 and 5% strengths reduced browning on the exposed surface, the polyphenol

TABLE 1.—*Effect of a citric acid dip on the browning reaction in steam-peeled green bananas*

Concentration of citric acid solution	Dipping time	Reaction to cathecol solution	Slices without browning after 10 min exposure
%/wt	*Min*		%
0	0	Heat ring active Inner pulp positive	54
1	5	Same	42
3	5	Same	100
5	5	Same	86

oxidase was still active in the inner pulp, resulting in browning while trimming or during accidental breakage of the bananas in processing.

Sulfitation

Sánchez-Nieva and Mercado (9) reported that steam-peeled bananas can be sulfited to levels of 400 p/m SO_2 by dipping for 8 min in a solution of 1% $K_2S_2O_5$ at room temperature. However, to be effective in controlling the browning reaction, sulfite uptake by the inner tissue should reach the level at which enzyme activity is blocked. Table 2 shows the sulfite uptake in the heat ring and core of bananas sulfited in 1% $K_2S_2O_5$ solution at pH 3.4. In slices 1½ in (38 mm) thick the heat ring showed a high SO_2 content after sulfiting for 4 and 6 min, but the remaining tissue has a low content of only 22 to 32 p/m. When the whole fruit was sulfited, no SO_2 was detected in the inner pulp.

Table 3 shows the diffusion of sulfite to the core of the fruit when dipping time ranged from 5 to 240 min in a 1% $K_2S_2O^5$ solution. This shows that sulfiting from 5 to 240 min resulted in a sulfite uptake by the whole slice which ranged from 334 to 1,289 p/m. The sulfite content of the core increased with dipping time, reaching a maximum of 308 p/m after sulfiting for 240 min.

The reaction of polyphenol oxidase with cathecol affords an excellent

TABLE 2.—*Sulfite uptake in heat ring and in core of sliced and whole steam-peeled bananas. Sulfitation in 1% $K_2S_2O_5$ solution, 5,568 p/m SO_2, pH 3.40*

Dipping time	SO_2 content in		
	Whole piece	Heat ring	Core
Min	*P/m*	*P/m*	*P/m*
	Slices 1½ in		
4	363	477	22
6	412	595	32
	Whole bananas		
4	255	370	0
6	241	381	0

TABLE 3.—*Effect of dipping time on SO_2 content of whole slice and core, and on inactivation of phenolases. Sulfitation in 1% $K_2S_2O_5$ solution, 5,650 p/m SO_2, pH 5.0*

Dipping time	Reaction to cathecol	SO_2 content in—		Radius of cross sectional area giving a positive cathecol test
		Whole slice	Core	
Min		*P/m*	*P/m*	*1/64 in*
5	+	334	0	18
10	+	397	0	15
15	+	468	0	15
20	+	515	15	18
25	+	959	91	18
30	+	985	56	18
40	+	1,118	108	12
50	+	1,279	86	12
60	+	1,354	116	10
120	+	1,582	311	10
180	+	1,130	232	5
240	+	1,289	308	5

method for determining sulfite penetration by fruit tissue (7). Slices with a level of 308 p/m SO_2 in the core tissue gave a positive test to cathecol, indicating enzyme activity. The data in table 3 indicate that even after sulfiting for 240 min, the polyphenol oxidase was still active in an area in the center of the fruits, with a radius of 5/64 in (2 mm).

Complete polyphenol oxidase inactivation resulted after sulfiting in 1% $K_2S_2O_5$ solution for 22 h. Bathia et al. (1) and Von Loesecke (10) had

previously reported a poor absorption of SO_2 from potassium metabisulfite solutions by bananas.

Table 4 shows the degree of browning resulting after the inner pulp of green bananas sulfited to different levels was exposed to air. In the unsulfited control samples, browning developed rapidly in 45 min of exposure to air. When the level of sulfite reached 235 p/m SO_2, no appreciable browning developed in 105 min. Increasing the level of SO_2 did not extend the time at which lack of browning was observed beyond 105 min.

Since there is the possibility that during thawing, as the ice melts and

TABLE 4.—*Effect of sulfite level on browning of internal tissue of steam-peeled green bananas*

SO_2	Degree of browning after exposure to air for time in minutes indicated[1]								
	15	30	45	60	75	90	105	120	230
P/m									
0	4	2	1						
60	4	3	3	3	2	2	2	1	
140	5	5	5	5	5	5	3	3	3
235	5	5	5	5	5	5	5	4	4
325–708	5	5	5	5	5	5	5	4	4

[1] Degree of browning: 5, no browning; 4, light browning; 3, moderate browning; 2, moderately strong browning; 1, strong browning.

TABLE 5.—*Effect of thawing on diffusion of sulfite from heat ring to core in 1½ inch slices*

Total SO_2 content	SO_2 content in core after thawing for			
	30 min	2 h	4 h	6 h
P/m	*P/m*	*P/m*	*P/m*	*P/m*
313	0	12	14	29
388	0	49	79	55
414	0	68	104	74
468	0	58	117	132

the tissue becomes softer, there might be a greater diffusion of sulfite to the inner pulp, the diffusion of sulfite to the core was measured for different levels of sulfite during thawing. The results of these tests, given in table 5, show that the sulfite content in the inner core increased with the sulfite content of the whole slice and with thawing time. Diffusion of sulfite to the inner pulp was slow, and at a sulfite level of 468 p/m SO_2, a level of only 132 p/m was reached in the inner pulp after thawing for 6 h.

When steam-peeled sulfited bananas which had been quick frozen were

cooked in boiling water until tender, no browning could be detected in the surface or on the inner pulp. This lack of browning is due to the facts that in the surface tissue, the polyphenol oxidase activity has been stopped by the sulfite treatment, and that cooking inactivates the enzyme in the inner pulp. Due to mishandling and inadequate storage temperature, however, frozen products may suffer alternate cycles of freezing and thawing during distribution and handling. Since the polyphenol oxidase in the inner pulp remains active after sulfitation, causing browning during thawing, sulfitation cannot be relied upon to protect green bananas from browning. Furthermore, there is a strong possibility that freezing green bananas with the oxidative enzymes active may result in off-flavor development during storage.

HOT-WATER PEELING

As previously indicated, whole bananas must be heated to an inner temperature of 197° F (91° C) to inactivate completely the polyphenolase.

TABLE 6.—*Effect of SO_2 level on browning of internal tissue of green bananas on exposure to air*

SO_2 level	Degree of browning after exposure to air for time indicated in min[1]								
	15	30	45	60	75	90	105	120	230
P/m									
0	4	2	1						
60	4	3	3	3	2	2	2	1	
140	5	5	5	5	5	5	3	3	3
235	5	5	5	5	5	5	5	4	4
325	5	5	5	5	5	5	5	4	4
472	5	5	5	5	5	5	5	4	4
552	5	5	5	5	5	5	5	4	4
708	5	5	5	5	5	5	5	4	4

[1] 5, no browning; 4, light browning; 3, moderate browning; 2, moderately strong; 1, strong.

When whole raw bananas of average plumpness are heated in water at 200° F (93° C) it takes 20 min for the temperature in the inner tissue to reach 197° F (91.5° C). This treatment loosens the peel, which can then be easily removed by hand. When the enzyme system was inactivated by dipping the raw fruit in water at 200° F (93° C), no browning was observed in any part of the fruit. Both the surface and inner pulp gave a negative polyphenol oxidase test with cathecol. Due to variations in finger plumpness and size, it was found that to assure enzyme inactivation in all fruits of a batch, heating should be extended to 30 min. The heating time required to inactivate the enzyme system by heat can be shortened to 20 min by processing in boiling water. However, due to the nuisance of steam produced by the boiling water in a processing plant, processing at 200° F is preferred.

Green bananas may also be steamed at atmospheric pressure to facilitate peeling and inactivate the enzyme system. The time required to heat the fruit in steam to 197° F (91.5° C) ranged from 10 to 18 min depending upon the plumpness of the fingers. When fingers of mixed size were steamed, it was necessary to heat for at least 18 min to inactivate the enzymes completely in all the fruit treated.

When steam treatment in a retort at 80 lb pressure and hot-water peeling of green bananas are compared, steam peeling has the advantage of saving 10 min or less time to steam the fruit and unload the retort. However, although hot-water peeling requires heating the fruit for 30 min, the facts that the enzyme system is inactivated, that no browning takes place, and that no additive such as sulfite need be used, upsets the apparent disadvantages resulting from a longer processing time. Besides, the hot-water-peeled bananas have smoother surface and better appearance than the steam peeled. Disregarding any other considerations, the peeling method to be chosen for peeling green bananas will depend on its effect on product quality and shelf life.

RESUMEN

Para pelar fácilmente los guineos verdes, éstos pueden tratarse con vapor a una presión de 80 lb. por 30 segundos. Este tratamiento inactiva la enzima polifenoloxidasa en la superficie de la fruta hasta una profundidad de alrededor de ⅛ de pulgada (3 mm), pero no en el tejido interno de la fruta. Un tratamiento más prolongado de calor con vapor a presión, así como la combinación del tratamiento al vapor con una escaldadura en agua caliente o al vapor no puede utilizarse para inactivar el sistema enzimático porque la fruta se ablanda más de lo deseable si ésta ha de congelarse.

El pardeamiento disminuyó en las superficies expuestas cuando la fruta tratada al vapor se sumergió por 5 min en soluciones de ácido cítrico al 3 y al 5%, pero este tratamiento no inactivó la polifenoloxidasa en el tejido de la fruta.

Cuando la fruta cortada en rodajas de 1½ pulgada (38 mm) de grosor se sulfitó en una solución acuosa de metabisulfito de potasa al 1% por 6 min, el contenido en SO_2 en la superficie subió a 595 ppm, pero en el interior fue de solo 32 ppm. Este tratamiento no inactivó la polifenoloxidasa en el interior de la fruta. Cuando la fruta entera se sulfitó el sulfito no penetró el tejido interno. Cuando se sulfitó al guineo verde en una solución a 1% de $K_2S_2O_5$ por 240 min el contenido total en sulfito llegó a un nivel de 1289 ppm, y a uno de 308 ppm en el tejido interno. Aun así, en el interior de la fruta, alrededor de los ovarios y las semillas, la polifenoloxidasa no fue inactivada. La fruta tratada con metabisulfito, con el sistema enzimático activo en el tejido interno, se pardeó bastante al deshelarse.

Cuando la fruta sulfitada se deshiela el sulfito se difunde hacia el tejido interno, y el nivel final de SO_2 depende de la concentración del sulfito y de la duración del período de deshielo. En fruta deshelada por seis horas, la difusión del sulfito hacia el interior no fue lo suficiente para inactivar la polifenoloxidasa en el tejido interno.

Tanto la inactivación completa de la polifenolasa como el pelado de las frutas se lograron calentándolas en agua a 200° F por 30 min. La fruta así tratada no se pardeó al ser expuesta al aire. La apariencia de la fruta tratada con agua caliente fue mejor a la de la tratada con vapor a presión.

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