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Lipoxygenase and Off-flavor Development in Some Frozen Foods

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일부냉동식품에서의 Lipoxygenase와 이취발생관계

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Abstract

Several tests were conducted to study lipoxygenase activity and off-flavor developement in frozen sweet corn.

Fresh corn contained about 60% of total lipoxygenase activity in the germ section. When non-blanched frozen sweet corn was stored at −10°F, it developed off-flavor and most significant changes in the fiavor profile of off-flavored sweet corn was 4~5 times higher hexanal peaks.

The high hexanal peaks observed in the sterilized sweet corn with added lipoxygenase, alone and in combination with other enzymes, suggested the fact that high hexanal peaks in off-flavored sweet corn could be due to an oxidative reaction of lionleic acid (and other unsaturated fatty acids) catalyzed by lipoxygenase. Based on lipoxygenase activity and linoleic acid content in sweet corn, this reaction occur most heavily in the germ section of sweet corn.

There was a significant relationship between flavor score of frozen stored corn-on-the-cob and hexanal peak in the germ section of corn-on-the-cob. This result indicated that hexanal peak could be used as an objective index of off-flavor development in frozen sweet corn.

Introduction

The quality of frozen foods is influenced by the condition of raw material used for freezing, freezing methods, post freezing handling and storage conditions. Chemical and physical changes in frozen foods take place slowly at the low temperature during storage, and these deteriorate the quality of forzen foods.

The most important physical changes which cause quality deterioration of frozen foods are recrystallization of ice and sublimation of ice. Recrystallization of ice and growth of ice crystals lead to texture change, and sublimation of ice on the surface of the product to freezer burn. Chemical quality changes, such as off-flavor development, discoloration, and loss of nutrients, also occur during storage of frozen foods. These chemical and physical changes are most significantly affected by the storage temperature and storing frozen foods below 0°F is generally accepted practice to minimize these changes.

Off-flavor developement in frozen plant foods is

related to enzyme activities and autoxidation of lipids. Vegetables are blanched prior to freezing to heat-inactivate enzymes in the tissue. Various enzymes have been suggested as causative agents in off-flavor develoment in frozen plant foods, but attention has been centered around catalase and peroxidase and used these two enzymes in the control of blanching treatment as an index of adequacy of blanching. However, there is no proof that these enzymes actually play a part in developing off-flavor.

Recently, lipoxygenase has been proposed as causative agent in the development of off-flavors and chlorophyll losses in underblanched frozen peas[1~3]. Lipoxygenase is highly specific for the oxidation of fatty acids which contain a cis, penta -1, 4-diene unit (—CH=CH—CH_2—CH=CH—). This enzyme is heat labile and found in a wide variety of plants, particularly in legumes. The objectives of this study are to investigate involvement of lipoxygenase in off-flavor developement of frozen corn, and to evaluate a relationship between objective off-flavor profile and sensory flavor score of frozen corn.

Materials and Methods

Test 1

Freshly harvested sweet corn (moisture content 72~75%) was frozen in Freon after preparation. Frozen sweet corn was divided into kernel section, outer cob section (including germ) and center cob section and subjected to enzyme analysis. Peroxidase activity was determined by the o-phenylene-diamine method[4] and lipoxygenase activity by a UV spectrophotometric method[5].

Test 2

Sweet corn was frozen in Freon with and without blanching at 210°F for 15 min. Frozen samples stored at −10°F for 6 months were subjected to gas chromatographic analysis, using 5% LAC-2R-446 as packing medium, to investigate changes in flavor profile due to off-flavor development.

Test 3

Fresh sweet corn kernels were filled in 303 cans with water and sterilized at 250°F for 40 min to inactivate enzymes and bacteria. Sterilized corn kernels were blended, and single and multiple enzymes were mixed with blended corn as shown below:

Single enzymes

Peroxidase : 14 *mg*/150 *g* of corn

Catalase : 6.25 *mg*

Lipase : 229 *mg*

Lipoxygenase : 80 *mg*

Multiple enzymes

Combinations of 2-4 enzymes

Each enzyme level in multiple enzyme treatements was the same as in single enzyme treatments. Corn and enzyme mixture was filled in 6 oz. cans, seamed and stored at −10°F for 8 months. Stored samples were subjected to gas chromatographic head space analysis.

Test 4

Sweet corn ears were blanched in a steam blancher at 210°F for 5, 7, 10 and 15 min. Blanched sweet corn ears were frozen in Freon and stored at −10°F for 9 months. Stored samples were used for flavor evaluation and enzyme analysis.

Results and Discussion

Distribution of enzymes in sweet corn

Peroxidase and lipoxygenase activities in sweet corn of 11 hybrids are summarized in Table 1. These samples were of similar maturity and all were harvested on the same day.

Table 1. Distribution of peroxidase and lipoxygenase in sweet corn

	Kernel section	Outer cob section	Center cob section
Lipoxygenase activity	3.1	9.2	3.6
% activity	19.5	57.6	22.6
Peroxidase activity	9.0	22.2	5.3
% activity	24.7	60.8	14.5

Notes (1) 1 peroxidase activity unit: changes in one optical density per 5 min per *g* of fresh sample.

(2) 1 lipoxygenase unit: changes in 0.1 optical density per min per *g* of fresh sample.

Lipoxygenase and peroxidase activities in the outer cob section(including germ) were 57.6% and 60.8% of total activities of each enzyme, respectively. There were no significant difference in lipoxygenase activities between the kernel and the center cob sections. Peroxidase activity in the kernel section was slightly higher than that in the center cob section.

Changes in flavor profile due to off-flavor development

Frozen sweet corn without blanching developed discoloration and off-flavor in 3 months of storage, whereas blanched sweet corn maintained good flavor during the storage.

The result in Table 2 showed that hexanal peaks in kernel and germ sections of non-blanched sweet corn were 4~5 times higher than those of blanched sweet corn. This result suggested that the high hexanal peak could be one of the most significant changes in flavor profile due to off-flavor development in sweet corn during frozen sotrage.

Table 2. Gas chromatographic flavor profile of frozen stored sweet corn

Sample	Peak height (*mm/g*)			
	DMS/acetaldehyde	Propanal	Ethanol	Hexanal
Kernel section				
No blanch	761×10^3	987×10^2	439×10^3	263×10^2
15 min blanch	548×10^3	674×10^2	594×10^3	49×10^2
Germ section				
No blanch	1284×10^3	1727×10^2	1092×10^3	230×10^2
15 min blanch	1108×10^3	1151×10^2	556×10^3	66×10^2

Note; DMS denotes dimethyle sulfide.

Flavor profile of enzyme treated corn

Flavor prefile of sweet corn as affected by various enzyme treatments was investigated by head space analysis using a gas chromatograph. Peak heights of DMS/acetaldehyde, propanal and ethanol did not significantly change with enzyme treatments. However, peak heights of hexanal significantly increased in samples with lipoxygenase, alone or in combination with other enzymes (Table 3).

Table 3. Gas chromatographic flavor profile of enzyme treated sweet corn samples stored at −10°F for 6 months

Sample	μg Hexanal/g sample
Control	0.16
Peroxidase (P)	0.15
Catalase (C)	0.17
Lipase (L)	0.16
Lipoxygenase (Li)	0.58
P-C	0.13
P-L	0.16
P-Li	0.62
C-L	0.16
C-Li	0.72
L-Li	0.54
P-C-L	0.13
P-C-Li	0.48
P-L-Li	0.54
C-L-Li	0.61
P-C-L-Li	0.53

The results showed that peroxidase, catalase or lipase did not markedly affect flavor profile of sweet corn samples.

Lipoxygenase catalyzes oxidation of unsaturated fatty acids, such as linoleic and linolenic acids, resulting in hydroperoxide. Hydroperoxide undergoes autoxidation and hexanal is an intermediate product of autoxidation.

Corn oil has large amount of linoleic acid (about 50% of total fatty acids of corn oil)[6], which is a good substrate of lipoxygenase. High lipoxygenase activity and high linoleic acid content in corn germ section would support the fact that off-flavor developed in frozen sweet corn during storage could be due to the reaction of lipoxygenase on linolei

acid (and other unsaturated fatty acids), resulting in formation of much hexanal as detected by gas chromatograph.

Heat inactivation of lipoxygenase and flavor quality of stored corn-on-the-cob (c-o-c)

Lipoxygenase activities, hexanal peak and sensory flavor score of frozen stored c-o-c are summarized in Table 4. Lipoxygenase activities in kernel and germ sections of c-o-c were negative after 7 and 10 min blanch at 210°F, respectively. Hexanal peaks in kernels of c-o-c blanched at 210°F did not change with blanch time, whereas those in germ section changed with blanch time(Table 4). The results showed that 10 min blanch at 210°F inactivated lipoxygenase in the germ section of c-o-c, as shown by lipoxygenase activities and hexanal peaks.

Sensory score of 9 months stored c-o-c was improved with increased blanch time. There was significant linear relationship between the sensory score and the hexanal peak in the germ section of stored c-o-c. These results indicate that the hexanal peak could be used as an objective index of off-flavor development in c-o-c during storage.

Table 4. Lipoxygenase activities, hexanal peaks and flavor score of frozen sweet corn (c-o-c) stored at −10°F for 7 months

Blanch time(min)	Lipoxygenase activities	Haxanal peak ($\mu g/g$)	Flavor score
5 Kernel	0.7	0.087	1.4
Germ	3.2	0.450	
7 Kernel	0	0.110	2.0
Germ	0.8	0.306	
10 Kernel	0	0.051	3.2
Germ	0	0.064	
15 Kernel	0	0.077	4.1
Germ	0	0.042	

Notes (1) Flavor score=3.948−5.909 (Hexanal in germ), r=0.96*

(2) Flavor scores : 5 ; as good as fresh prepared corn, 1 ; unacceptable.

요 약

냉동 단옥수수에서 발생되는 이취와 lipoxygenase 역가간의 관계를 규명하기 위하여 여러가지 시험이 수행되었다.

수확직후 단옥수수의 lipoxygenase 역가는 전체의 약 60%가 배아부분에 있는 것으로 나타났다. 자숙하지 않은 채 단옥수수를 냉동 저장했을 때 저장중에 이취가 발생되었으며, 이취가 발생된 단옥수수의 flavor profile 중 가장 중요한 변화는 대조구에 비하여 4~5배 높게 나타난 hexanal peak였다.

살균 처리한 단옥수수에 lipoxygenase를 단독 또는 다른 효소와 혼합하여 첨가한 처리구에서 높은 hexanal peak가 관찰되었는데, 이런점으로 미루어보아 이취가 발생된 단옥수수의 높은 hexanal peak는 리놀레산(그리고 기타 불포화 지방산)이 lipoxygenase의 촉매작용으로 산화된데 기인하는 것으로 여겨진다. Lipoxygenase의 역가와 리놀레산 함량분포를 근거로 관찰해 보면 이런 산화작용이 대부분 배아부분에서 일어난다고 할 수 있겠다.

냉동 저장한 대공에 붙은 단옥수수(corn-on-the-cob)의 관능시험결과와 배아부분의 hexanal peak간에는유의성이 있는 상관관계가 있었으며, 이런 결과는 냉동 단옥수수의 이취발생여부를 객관적으로 측정하는 방법으로 hexanal peak를 사용할 수 있음을 말해준다.

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