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Study on the improvement of color quality of dried squid product

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[課程博士・論文博士共通]

博士学位論文内容要旨 Abstract

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論文題目 Title	Study on the improvement of color quality of dried squid product (イカ肉乾製品色調改善法の開発に関する研究)		

Squid is common seafood consumed in Japan as *sashimi* or as a variety of processed foods and is popular because of its special flavor. Dried squid (*surume*) is a very popular snack food with both Japanese adults and children because of its unique flavor and taste. Moreover, it is easily stored because of its low moisture content. The appearance, especially the surface color is a primary factor determining the value of dried squid products. Brown discoloration occurred during processing and subsequent storage is a serious problem and reduces the value of the products. Previous study suggested that the brown discoloration is caused by Maillard reaction.

Japanese common squid (*Todarodes pacificus*) is a dominant squid species in the Japanese fishery industry. However, the squid is known to discolor easily, and this is one of the problems in seafood processing industry. Therefore, to clarify why mantle meat from Japanese common squid undergoes a high degree of browning during air-drying, the mechanism study of high browning degree of mantle muscle meat from Japanese common squid was conducted by comparison with long-finned squid (*Photololigo edulis*) and bigfin reef squid (*Sepioteuthis lessoniana*).

The squid mantle meat was ground using a meat chopper. The homogenate was dried on rimmed silicon plate at 40 °C for 11 h. The factors contributing to the browning of three species squid were investigated by surface color, protein composition, reducing sugar content, and free amino acid composition in boiled and raw meat before and after air-drying. The Maillard reaction occurred in ground mantle meat from the three types of squid during air-drying was investigated using a sugar-amino acid model. Significant brown discoloration of Japanese common squid meat was observed when compared with other squids, whereas, it was mitigated when the meat was boiled before drying. Japanese common squid meat contained much higher concentrations of ribose and arginine (Arg) than the other squid meats did. The FAAs were generated during the air-drying of raw meat, whereas the generating of FAAs was suppressed in boiled dried sample. The model solutions of squid meat indicated that the reaction between ribose and Arg may be a key factor of brown discoloration during air-drying. Those suggest that the reason why Japanese common squid discolors significantly more than the other two species did during air-drying is its high contents of ribose and Arg and the high protease activity.

The role of endogenous protease(s) on brown discoloration during the processing of dried squid products was studied as a next step. The squid mantle meat was added various proteinase inhibitors before dried, and evaluated for its surface color, Maillard reaction degree, protein composition and FAAs content. Furthermore, the squid meat homogenate was used to further clarify the characteristic of endogenous protease(s) involved in generating the FAAs. The brown discoloration were obviously mitigated by adding metalloproteinase inhibitor, especially ethylene glycol-bis (2-aminoethylether)-N,N,N',N'-tetraacetic acid (EGTA) and 1,10-phenanthroline, followed by serine proteinase inhibitor, especially phenylmethanesulfonyl fluoride (PMSF). In both of dried squid product and the homogenate, the addition of EGTA, 1, 10-phenanthroline and PMSF prevented degradation of myosin heavy chain and increase of the FAAs including Arg which belongs to basic amino acids. All results indicate that endogenous metalloproteinase and serine proteinase influence the generating of FAAs including Arg which contributes to brown discoloration during air-drying process.

In food factory processing, the chemical reagents, such as 1, 10-phenanthroline and PMSF are not permitted to be used as food additives. It is necessary to find a protease inhibitor which is permitted as a food additive. Organic salts, as a kind of food additives, some of them are known to inhibit the autolysis of squid muscle meat via chelating ability. Therefore, to identify the effect of organic salts on the brown discoloration of dried squid product during air-drying, 5 types of organic salt were added to Japanese common squid meat before air-drying and compared their effect with EGTA and EDTA. From the results of surface color and Maillard reaction degree, it was clarified that organic salts, especially Na-citrate and Na-phytate could prevent the brown discoloration of squid products during air-drying. Among organic salts, Na-citrate and Na-phytate showed high ability to inhibit the autolysis of squid mantle muscle proteins and the generating of FAAs including Arg in both squid product and homogenate. Na-citrate showed the highest inhibitory activity similar to that of EGTA, followed by Na-phytate. These results indicate organic salts could prevent brown discoloration of Japanese common squid dried product by inhibiting protein degradation and FAAs generating, which are involved in Maillard reaction of squid products during air-drying.

Furthermore, the effect of pH on the brown discoloration of dried squid products were investigated by adjusting squid meat pH from 4~9 before air-drying. The brown discoloration was significantly mitigated when adjusting meat pH to acidic condition, especially pH 5.5, contrasted with accelerated at alkaline condition, especially at pH 8. pH 5.5 was considered to optimal pH for dried squid meat processing because of its lowest proteases activity, FAAs generating including Arg and reactivity of Maillard reaction. More generating of Arg and high reactivity of Maillard reaction test was confirmed to occur at alkaline meat samples, even reached to the maximum at pH 8. Moreover, the low Arg generating rate and reactivity of Maillard reaction at acidic condition was the reason of samples at pH 4 and 4.5, which were not observed remarkable brown discoloration but determined the highest proteases activities, strongest protein degradation and most total FAAs.

All results indicated that the drastic brown discoloration occurred during the processing of Japanese common squid meat caused by its high endogenous metalloproteinase and serine proteinase activities, as well as high ribose contents and generating of FAAs including Arg. Before air-drying, adding organic salts such as 1% Na-citrate and Na-phytate, or adjusting pH value to acidic condition especially pH 5.5, could successfully mitigate the strong brown discoloration during air-drying processing. The study cloud provides basic data and is applied to industrial production of dried squid.