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Changes of Patulin Concentration in Apple Products During Processing Stages: A Review

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Abstract

Researches on the therapeutic properties of apples and their products have been drawing attention recent years. Their therapeutic features provide an increase on the popularity of these products and their consumption has a protective effect against certain disorders. Weight loss products made from apples and apple products in use among the public bring out an important risk of patulin. Patulin may occur in apples during harvest and post harvest stages. Process stages and stage conditions may cause an increase or decrease in patulin concentrations. Most of the time, it is impossible to prevent the product from patulin formation. Nature of the process steps such as fermentation, heat treatment and clarification applications or additional steps of production line such as gamma irradiation or application of binding material can help remove patulin from products or reduce its concentration with the lowest cost. In this study, patulin concentration changes are explored during the production processes of apple products according to scientific researches.

Key words: Patulin, mycotoxin, detoxification, apple product

Elma Ürünleri İşleme Aşamalarında Patulin Konsantrasyonunda Meydana Gelen Değişimler Üzerine Bir Derleme

Özet

Elma ve ürünleri üzerinde son yıllarda yapılan araştırmalar bu ürünlerin terapötik özelliklerine yoğunlaşmıştır. Elma ve ürünlerinin sahip olduğu terapötik özellikler bu ürünlerin popülaritesinde ve tüketiminde artışlar sağlamıştır. Hastalıklara karşı koruyucu etkisi ve zayıflama ürünlerinde kullanımı ile halkın dikkatini çeken elma ve ürünlerindeki en önemli risklerden bir tanesi patulin riskidir. Bahçe, hasat ve hasat sonrası şartlarda oluşma riski olan patulinin, üretim süreçlerindeki aşamalara ve bu aşamaların koşullarına bağlı olarak konsantrasyonunda artış veya azalış gözlenmektedir. Çoğu zaman patulinin oluşmasının engellenmesi pek mümkün olamazken, üretim aşamalarının doğası gereği uygulanan fermantasyon, ısıl işlem, ve filtrasyon uygulaması gibi işlemlerle veya ışınlama, bağlayıcı madde uygulaması gibi üretim hattına ilave işlemler eklenmesi ile patulinin üründen uzaklaştırılması veya indirgenmesi düşük maliyetle ve daha kolay şekilde gerçekleştirilmesi araştırılan konulardandır. Bu araştırmada elmadan elde edilen ürünlerin üretim süreçlerindeki patulin içeriklerindeki değişimler, bu değişime neden olan faktörler ve patulin detoksifikasyonunda kullanılan yeni teknikler bilimsel veriler ışığında irdelenmek istenmiştir.

Anahtar Kelimeler: Patulin, mikotoksin, detoksifikasyon, elma ürünleri

INTRODUCTION

The mycotoxin patulin (Figure 1) is a toxic secondary metabolite produced by a wide range of fungal species of the Penicillium, Aspergillus and Byssochlamys genera [1,2]. *Penicillium expansum* is frequently found as a postharvest contaminant in apples and apple products and it is responsible from the production of patulin in apple and apple product [3]. The mycotoxin patulin was first described in 1942 as a potentially useful antibiotic with a wide spectrum of antimicrobial activity. It was discovered several times during screening programmes for novel antibiotics. It was not until 1959 that an outbreak of poisoning of cattle, being fed on an emergency ration of germinated barley malt sprouts, alerted the veterinary profession to patulin as a mycotoxin [4].

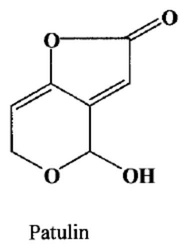

Fig.1. Chemical stucture of patulin

The natural contamination with patulin of apple products, including juices, has been reported in different studies carried out in several countries [1, 5, 6].

A provisional maximum tolerable daily intake (TDI) of 0.4µg/kg body weight has been set [7]. Based on this TDI, patulin is regulated in the European Union (EU) at levels of 50µg/kg in fruit juices [8], ingredients in other beverages, spirit drinks, ciders and other fermented drinks derived from apples, 25µg/kg in solid apple products and 10µg/kg in apple-based products for infants and young children [9].

Penicillium expansum causes a soft rot of apples and although the rot itself is typically soft and pale brown. This particular species has a special significance because of its ability to produce the mycotoxin patulin which has been detected as a contaminant in unfermented apple juices [4]. Processing can play an important role in reducing the potential risks of mycotoxin-contaminated food commodities [10]. Bu it is difficult to destroy patulin in products made from apples because patulin is relatively heat-stable and tolerant to acidic conditions. Therefore it is very important to remove any apples or parts of the apple that are contaminated with patulin before processing [11]. Patulin has also become important to apple processors as a method for monitoring the quality of apple juices and concentrates. The presence of high amounts of patulin indicates that moldy apples were used in the production of the juices. For that reason the problem of detecting low levels of patulin in apple juices continues to receive attention [12].

The objective of this study was to present the effect of some stages of apple product processing (milling, pasteurization, enzymatic treatment, micro filtration, fermentation and evaporation) on patulin concentration. Also the uses of some new techniques to remove the patulin from apple products reported in the latest scientific researches.

Patulin Concentration Changes In Production Stages

Historically, apple juice has been a product of high concern with regard to patulin contamination. Therefore, many of the investigations on patulin stability during food processing have focused on apple juice [13]. All stages of apple juice production contributed to patulin reduction. Apple selection is a preventive measure to control safety hazards and good manufacturing practices in apple juice production can effectively reduce contamination [10]. Patulin is not found in intact fruit because it is damage to the surface of fruit that makes it vulnerable to Penicillium infection [13]. Thus, the critical point for controlling fruit quality is the point at which the fruit enters the processing line [14].

The occurrence of patulin in fruit juices is bound to several factors. Both fungal growth and mycotoxin production depend on environmental factors such as temperature and water activity [15]. In addition, present practices in fruit cultivation and juice making have a great impact on the occurrence of patulin in fruit juices [16]. It is well known that the use of fungicides can reduce the mold development. By contrast, it has been demonstrated that a long time period of outdoor storage between harvest and processing, dramatically increased the patulin levels in apple fruits [17]. Patulin is a water-soluble compound and have low molecular weight. It is potentially capable of diffusing from the decayed portion to the visibly unaffected areas [18].

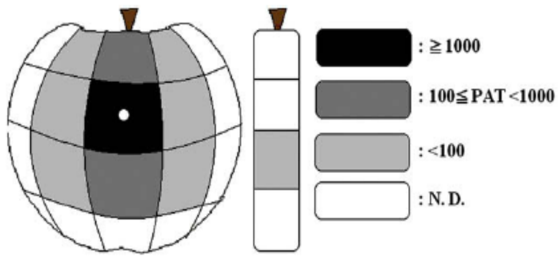

Fig.2. Distribution of patulin in P. expansum inoculated apple. White dot in dark portion: place P. expansum was inoculated. Ten apples treated same way and analyzed as one sample (Patulin:PAT, Non Detected:N.D.) [11].

Removing the patulin contaminated parts of the apple can help to reduce the patulin contamination at minimal level in final product with minimal raw material losses [11].

The mean patulin level in the non-processed fruit was found to be 920 *ng/g*, but this level dropped to 190 *ng/g* following an initial water treatment step. Analyses of the wash water showed that appreciable levels had been transferred from the solid to the aqueous phase [19]. Washing and handling were critical steps in reducing patulin in apples since up to 54% could be removed by high pressure water spraying [20]. Additional removal, by hand, of rotten and damaged fruit prior to further processing, significantly reduced the mean patulin level in the juice to 55 *ng/g*. Mycological analyses tended to support the chemical data, in that removal of the rotten fruit significantly reduced the total fungal counts in the juice samples [19].

In industry scale production of apple juice concentrate, conventional clarification using a rotary vacuum pre-coat filter was more effective than ultra filtration. Losses were respectively 39% and 25% [20, 21].

The use of four different processes; fining with bentonite, pectinase treatment, paper filtration and centrifugation are examined. Reduction of patulin was shown to be due to binding to solid substrates. Centrifugation proved the most effective, removing 89% of the patulin [22]. Also charcoal is effective in achieving some reduction of patulin concentrations [23].

The patulin reduction achieved after enzymatic treatment using pectinase was 28.3%. After microfiltration process the mean loss of patulin was 20.1% [10]. This reduction on patulin levels can be attributed to the binding of the patulin to solid substrates that are removed with the microfiltration. It is thought that the pH of the apple juices lends heat stability to patulin, accounting for the variability in results. Because of this, it is important to assess the effectiveness of conditions specific to each process before implementing a process control measure [14]. The mean of patulin reduction achieved by evaporation was 14.1% in apple juice production when evaporation process was done at 80°C for 20 min [23]. Also can be reached 28.4% reduction in patulin level at 96°C for 30s [10]. Pasteurization was the stage of apple juice production that further contributed to reduction of patulin levels. Thus, the presence of patulin in fruit products, such as juices, may be used as an indicator of the quality of the product [12]. The overall loss of patulin through processing from apple to apple juice was 75.2%. When apple juices concentrate were diluted to consume, from 69 to 12 Brix with dilution factor of 4.75, the mean patulin concentration was found to be 21 ± 9.1µg/L, ranging from 15 to 46µg/L [10].

There is little information in the literature dealing with the analysis of patulin in dried solid apple products [24, 25]. Total ion Chromatograms of apple juice and dried apple samples which were purchased in Japan market places shown in figure 3.

A number of studies have shown that patulin is generally unstable during fermentation so that products such as cider and wine are usually free of patulin but the identity of any breakdown products has not yet been established exactly [26, 27, 28]. It is likely that when patulin is reported in cider this is the result of the addition of apple juice to produce sweet cider [21]. Significant reduction of the toxin can be achieved during fermentation, and the rate of disappearance is dependent, among other factors, on the yeast strain and the medium [29]. Complete destruction of patulin can be shown after fermentation for 48 hours or by treatment with 0,125% sulphur dioxide [30]. Also patulin was unstable in a study of the fate of [14C]-labelled patulin during the alcoholic fermentation of apple juice with *Saccharomyces cerevisiae* [26]. High performance liquid choromatograhy analysis of the fermentations showed the appearance of two major metabolites, probably E- and Z-ascladiol [21].

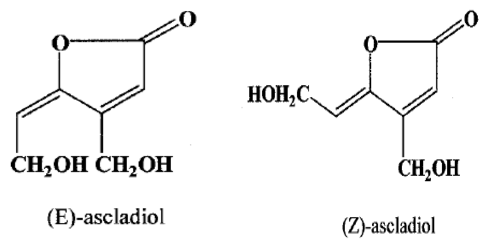

Fig.4. Chemical structure of reduction products of patulin, (E)- and (Z)-ascladiol.

In home-made apple jam which had become mouldy during storage, patulin was found to diffuse to all levels of the jam. So that patulin risk in home-made apple products appears to be greater than in commercial apple products [31]. There is some information about the thermal destruction rates for patulin and half-lives of patulin during the production of blackcurrant, blueberries and strawberries and berry jams in the literature [32] but there is no information about the changes of patulin in apple jam production steps.

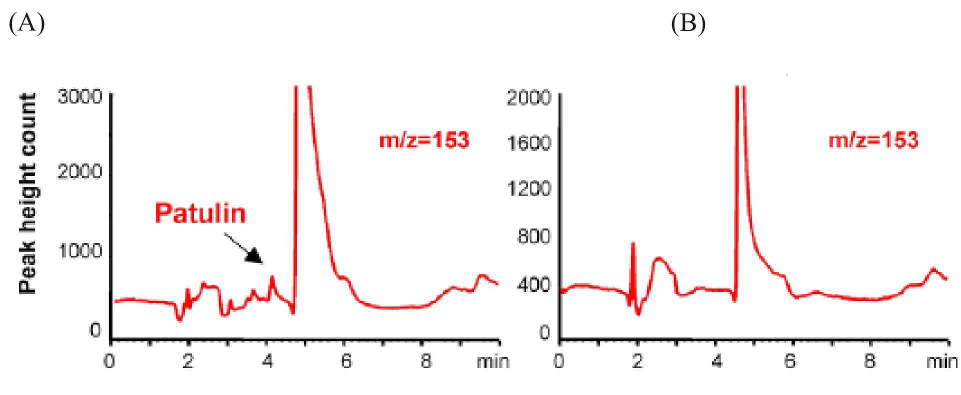

Fig.3. Total ion Chromatograms obtained from apple juice and dried apple samples by in-tube SPME LC–MS. (A) Apple juice (0.1mL) including 13.9ng/mL patulin; (B) dried apple (100mg) [25].

PATULIN REMOVING TECHNIQUES

The amount of the toxin can be markedly reduced by including the processing in simple and feasible means, applied separately or preferably in a combined treatment, thus ensuring that safe products reach the consumer [29].

Removal of patulin can be achieved by binding to materials used during processing, e.g., charcoal and composite carbon. Additives added to apple products may reduce their patulin content, but in some cases the quality of the product was adversely affected. Patulin destruction by additives in food products is dependent, among other factors, on temperature and length of storage [33]. Some indigestible adsorbents may adsorb the mycotoxins and so that they are not absorbable in the digestive tract. Such adsorbents are used in some feed supplements; e.g. a successful adsorption of patulin on activated carbon has been reported [34]. The possibility of adsorption of important micronutrients is the potential disadvantage of such methods of detoxification.

Boiling in 15% sodium hydroxide was a very effective means of removing patulin from damaged apples. These treatments can achieve a significant reduction in the patulin contamination of apple products [11, 35]. However, alkaline treatment can impair the taste of the final product and little is known about the degraded compounds derived from patulin formed by alkaline treatment. For this reason alkaline treatment is not a commercial option.

Patulin in apple juice decreases by the addition of ascorbic acid. Because patulin was decomposed by free radicals which were generated by the oxidation of ascorbic acid to dehydro-ascorbic acid, and the rapid oxidation of ascorbic acid. Rapid oxidation was catalyzed by free metal ions. All these processes resulted in a decrease of patulin [36, 37]. On the other hand, although malic acid, the main element of organic acid in apple, accelerated the degradation of patulin in the radio-degradation aqueous model system, patulin was stable in the apple juice. This result indicated that the natural degradation of patulin depends not on a single factor (malic acid) but on the nature of the complex reaction environment [38]. The previous studies reported that patulin is more stable against heat or chemicals in a condition of low pH [36]. Therefore, it is supposed that the degradation of patulin by radiation is influenced by the action of organic acids and amino acids, the elements that decrease pH in the apple juice [38].

Gamma irradiation could reduce patulin concentration in apple juice. However, this result was limited to apple juice model system only. Also the effects of ionizing radiation on chemicals depend on the nature of the environment [39]. Patulin in the apple juice was decomposed at 2kGy of gamma radiation. Patulin was relatively stable against radiation in the aqueous solution containing lactic acid, ascorbic acid, and histidine, but apple contains these elements in very small amounts [40]. The increase of patulin stability to gamma radiation in the apple juice because of malic acid, and serine and threonine may play a partial role. Also the low-pH condition might be responsible for the resistance of patulin against radiolytic degradation of apple juice by gamma irradiation [38].

CONCLUSION

Apple processing can be considered as an application with any combination of chemical, biological or physical methods used to produce final product. There are many factors that influence the amount of mycotoxins present during processing and understanding these factors will assist in maximizing their elimination ensuring that, as far as possible, no toxic reaction products are produced. There are lots of studies about the patulin concentration changes during apple juice production. But there is no or little information about the patulin concentration changes during the apple marmalade or jam, apple cider, sweetened apple cider and dried apple production. So that, new research areas about patulin in apple products should be carried out in these products. Also, studies should be carried out on establishing the new applications in production lines to reduce the patulin concentration in apple products.

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