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Effect of Sulphurization Process on Vitamin, Phytosterol and Fatty Acid Levels of Some Apricot Cultivars Grown in Turkiye

Fethi KAMIŞLI[1]*, Nazlı Gülüm MUTLU[2]
[1*] Department of Chemical Engineering, Faculty of Engineering, Firat University, Turkey.
[2]Department of Occupational Health and Safety, Faculty of Health Sciences, Bingöl University, Turkey.

[1*]fkamisli@firat.edu.tr, [2]ngmutlu@bingol.edu.tr

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Abstract: Two kinds of fresh apricot (Prunus armeniaca L.) samples were sulphurized in various concentrations of sodium metabisulfite solution at different immersion times. The sulphur contents in fresh apricot samples and in the apricot samples dried in open air for a week were determined as a function of immersion time. Variations of vitamins of K1, D2, E and phytosterols were determined as a function of sulphur content of two kinds of fresh apricot samples. It was observed that amount of vitamins of K1, D2 and E decreased with increasing concentrations of sodium metabisulfite solution and prolonging immersion time. Moreover, it was observed that there was no regular relationship between sulfur content and phytosterol changes in both apricot samples. While fatty acids such as palmitic acid, myristic acid and oleic acid were determined in all apricot samples, the palmitoleic acid, stearic acid and arachidonic acid were encountered in some samples.

Key words: Apricot, sulphurization, vitamins, physterols, fatty acids.

Kükürtleme İşleminin Türkiye'de Yetiştirilen Bazı Kayısı Çeşitlerinin Vitamin, Fitosterol ve Yağ Asidi Düzeyleri Üzerine Etkisi

Öz: İki çeşit kayısı örnekleri farklı daldırma sürelerinde çeşitli Sodyum metabisülfit konsantrasyonlarında kükürtlendi. Taze ve açık havada bir hafta kurutulmuş kayısı örneklerinin kükürt içerikleri daldırma süresinin fonksiyonu olarak belirlendi. İki çeşit kayısı örneklerinin kükürt içeriğine bağlı olarak K1, D2 ve E vitaminlerinin ve fitosterollerin değişimleri saptandı. Sodyum metabisülfit konsantrasyonunun ve daldırma süresinin artmasıyla K1, D2 ve E vitaminlerinin miktarlarının azaldığı gözlendi. Ayrıca, her iki kayısı örneklerinde de kükürt içeriğiyle fitosterol değişimleri arasında düze[1]nli bir ilişkinin olmadığı gözlendi. Palmitik asit, miristik asit ve oleik asit gibi yağ asitleri bütün kayısını numunelerinde saptanırken, pamitoleik asit, stearik asit ve araşidonik asit bazı kayısı örneklerinde bulunmuştur.

Anahtar kelimeler: Kayısı, Kükürtleme, vitaminler, fitosteroller, yağ asitleri.

1. Giriş

Apricot named as Prunus armeniaca L. which can be produced in the various parts of the World is one of the most important fruits. Apricot cultivation depends upon the soil compositions, its variety and climate conditions. The nutrition values, quality and yield of the apricot depend on processing method, variety, climate conditions and soil composition where apricot trees are cultivated. Apricot can be considered an important foodstuff on account of the nutrients and its minerals. Since the harvest period for apricots is short and the fresh apricots are quickly deteriorated, the large amount of apricot all over the world has to be consumed in fresh or be conserved with some preservation method to consume later. Therefore, some preservation methods such as drying and treatment with some chemicals are necessary to consume this fruit in different times and places from its producing time and place. It is reported that 20-25 % of the fresh apricots around the world are dried and processed products of the canned apricots, apricot jam, nectar marmalade, jelly and cream [1]. By preservation of this fruit, the economic loss of the fruit can be decreased and nutrition loss can be protected. The preservation methods will most likely protect the perishable foodstuff from spoilage and supply economic value by exporting. The drying of foodstuff with and without pretreatment prevents or retards microbial or non-microbial spoilages. The pretreated apricots with the sulphur contained substances should be dried since water dependent activities can be either prevented or retarded by drying process and Millard reactions can be either prevented or retarded by sulphurization. Moreover, the drying period of time is shortened for the pretreated apricots since shells of apricots are injured during sulphurization, allowing to remove moisture easily. The sulphurization that can be done by sulphur dioxide, bisulfites and metabisulfites is one of the most important effective methods used to prevent or retard browning reactions in the foodstuffs. Although the sulphurization prevents or retards browning reactions in the foodstuff, it should be done

*Corresponding author: fkamisli@firat.edu.tr, ORCID numbers of authors: [1]0000-0002-1769-3785, [2]0000-0003-0210-5175

carefully since sulphur content in apricots is necessary to be less than 2000 ppm that is a maximum allowable value.

Enzymatic and non-enzymatic reactions can take place during drying and storage of apricots. The formation of intermediate carbonyl products owing to series reactions in foodstuff can be called as non-enzymatic browning reactions that result in undesired brownian pigments with polymerization. The formed intermediate carbonyl products and reducing sugars react directionally with sulfites during the non-enzymatic reactions to prevent melanoids of those intermediate products. Ascorbic acid called as the reducing substance in enzymatic Brownian reactions inhibits color deterioration by reducing the o-kinons to the o-phenols while the ascorbic acid cracks down. The amount of ascorbic acid should be more than enough in reaction medium since ascorbic acid is consumed out, there will be no inhibitors on browning reactions. Furthermore, the ascorbic acid is consumed out by the oxygen having important role in browning reactions that can be retarded with reduction of the oxygen in reaction medium. Glaucous and fructose having, respectively, free aldehydes and ketones are called as the reducing sugars. The nutrition value of the foodstuff can be decreased with Millard reaction reducing sugar with proteins or amino acids.

In apricot drying, the sliced, halved or whole samples of apricot are commonly exposed to either directly to sun lights or conventional hot air that can be heated by sun lights ([2], [3]). Drying process and pretreatment of apricot samples affect quality of apricot, which is subject of several researchers ([4], [5], [6]). Horoz et al. [7] used hot air and microwave together to dry apricot samples in which quality of the dried apricot samples was compared with conventional drying process and it is claimed that the quality of apricot dried in the combined drying process (hot air +microwave) is better than that of the dried in conventional method. Albanese et al. [5] used hot air and infrared together to dry apricot in which quality of dried samples was compared with the sun drying apricot and it was claimed that the quality of apricot dried in this process is better than those dried in the sun lights. The combined drying process for the sulphurized and unsulphurized apricot samples was investigated by Ozbek et al. [8] to determine difference from the conventional drying method/methods in terms of hardness, color, retention of vitamin C, antioxidant activity, total phenolic content and β-carotene of apricot samples. According to food legislation, the allowable largest sulphur content is 2000 mg/kg (ppm) in dehydrated fruits. The sulphur dioxide preserves the texture and color of apricots and thus taste characteristics by inhibiting browning reactions and microbial deteriorations, which makes the dried apricots attractive to the consumers. It was reported by Pala et al. [9] that the amount of carbon hydrates, protein, oil, moisture, cellulose, total acid and ash in apricot depend upon variety of the apricot. Belloso and Barrichero [10] stated that some kinds of apricots are more suitable for drying to give vitamins, high calorific values and mineral rich products. The contents of minerals, vitamins, appearances and calorific values affected by the preservation method namely sulphurization and drying processes determine the quality of a foodstuff. Vitamins A, E and C having antioxidant roles against oxidative damage and cofactors for many enzymes must be taken into body ([11], [12], [13]).

In the sulphurization process, the fresh apricot can be sulphurized with either water soluble sulfite salts such as $Na_2S_2O_5$ and $K_2S_2O_5$ or sulphur dioxide used to preserve their color and to exterminate microbial agents that cause spoilage. The apricot samples are dried in open-air sun drying before and after removing stones from apricot. Pizzoferrato et al. [14] reported that sulfites are converted into the harmless products such as sulfate ions by oxidizing or removing from the foodstuff by evaporating. Polyphenol oxidase activity is prevented by decreasing pH of the solution used for sulphurization of apricot lower than 4.2 [15]. On the other hand, non-enzymatic browning reactions were accelerated in alkaline solution or neutral medium [16]. It was reported that the prevention of the browning reactions of litchi pericarp can arise from inhibition of polyphenol oxidase activity and stabilization of anthocyanins. Non-enzymatic and enzymatic browning reaction in vegetables and fruits can be prevented by sulphurization process ([17], [2]). The formation of H_2SO_3 increases with increasing sulphur concentration in the treatment solution, which results in values of larger titratable acidity [18].

In none of the reviewed papers, the variations of K1, D2, E and phytosterols in two kinds of apricot samples locally known hacihaliloglu and kabaaşı with concentrations of sodium metabisulphite (SMBS) solution and immersion times and thus, sulphur contents were not investigated. Therefore, in this study, variations of K1, D2, E (α-tocopherol and σ-tocopherol) vitamins and phytosterols as a function of immersion time were examined for various concentrations of SMBS solution. Moreover, amounts of fatty acids such as the myristic acid, oleic acid, palmitic acid, stearic acid palmitoleic acid and arachidonic were tried to determine in all apricot samples sulphurized in various concentrations of SMBS solution at different immersion times.

2. Material and Method

The chemicals used in the sulphurization and titration preprocesses were 37 % HCI, $Na_2S_2O_5$, 35% H_2O_2, NaOH, Brome phenol, Ethyl alcohol that were in analytical grade and purchased from Sigma Chemical Co. (Darmstadt, Germany).

Two different kinds of apricot samples locally known as hacihaliloglu and kabaaşı (Prunus armeniaca L.) existed in the apricot research center in Malatya, Turkey were collected in the same side of the tree with the same size, the same ripeness (pH = 4.25-4.35 for hacıhaliloglu, pH = 4.30-4.50 for kabaaşı) and the same appearance for each kind of the apricot samples to use in the experimental study. The harvested apricots samples were put into plastic bags and transferred to the laboratory and the apricot specimens in the plastic bags were kept in refrigerator at 5 °C. pH of fresh hacihaliloglu and kabaaşı apricot samples was measured to be in ranges of 4.25-4.35 and 4.30-4.50, respectively. In order to measure pH values of apricot samples, the apricot samples were homogenized in the homogenizer having three fold the distilled water of the apricot weight and the mixture was filtered using Whatman No.1 filter paper. The pH values of the apricot samples were measured using Mettler Toledo Delta pH meter.

The hacıhaliloglu apricot is one of the important apricot type to dry in Malatya, Turkey. This fruit has an average size (25 -35 g) in yellow color with reddish cheek and less water content, and shell of this fruit is thin and it is a luscious fruit. Kabaaşı apricot type has a large size (30-45 g) with oval and symmetric shape and the shell of this fruit in the yellow color is thick and it is a very luscious fruit.

All apricot samples used in the study were sulphurized with sodium metabisulfite ($Na_2S_2O_5$) that releases SO_2 when it dissolves in water. In other words, it forms sulphurouse acid (H_2SO_3), bisulfite $(HSO_3)^{-1}$ and sulphur three oxide $(SO_3)^{-2}$ in water. Sodium metabisulfite ($Na_2S_2O_5$) solutions were prepared in various concentrations namely 5, 15 and 20 % (w/v) to sulphurize apricot samples at different immersion times.

After sulphurization with various concentrations of sodium metabisulfite (SMBS) at different immersion times namely 15, 45, 60 and 90 minutes, all apricot samples were dried in open air for a week to determine the effect of drying process on the sulphur content of the apricot samples. As it is known, the drying, one of the oldest preservation method, is used to preserve food stuffs since beginning of human's history. The water content of food decreases with drying times and thus, water-dependent microbial deterioration in the food stuff is either decreased or entirely preserved with decreasing water activity [19]. In this study, the apricot samples were taken out from immersion utensils and placed on the cloths to be dried in open air. After three days of the drying, the stones of apricot samples were taken out and the apricot samples were shaped by hands and the shaped apricot samples were left to be dried in the open air for another four days. The dried apricot samples were put into the sterilized bags and closed carefully and then placed in a deep freeze at -60 °C and kept in there until being analyzed for determining sulphur contents of apricot samples.

3. Sulphur, Vitamins and Fatty Acids Analysis

3.1.1 Determination of sulphur in the apricot samples

The 5 g apricot sample treated with the certain concentration of SMBS solutions and certain immersion times were taken into homogenizer and made it slurry with 50 ml the distilled water. This slurred apricot sample (homogenized sample) was put in a round-bottom flask and 40 ml 15 % HCI was added into it. All remains of slurred apricot sample were transferred to the round-bottom flask by washing homogenizer with 100 ml distilled water. The flow of N_2 was adjusted to be 40 bubbles per minutes in the round-bottom flask since flow rate of N_2 is the most critical factor in performing experiment. N_2 and the releasing gas consisting of SO_2 and SO_3 were taken into 10 ml of 3 % H_2O_2 solution in a trap tube connected to the outlet of a condenser. The mixture (homogenized apricot sample + distilled water + 15 % HCI) in the round-bottom flask was boiled under the condenser mounted on the top of the round-bottom flask for 60 minutes to release sulphur compounds in the sulphurized apricot samples. The homogenized apricot samples were boiled in the presence of HCI to release the sulphur compounds in the apricot samples since HCI solution damages the structure of apricots [15] and damages become more pronounced by increasing acid concentration and temperature [20].

The reaction being taken place in the trap tube containing 10 ml of 3 % H_2O_2 solution can be written as in Equation (1).

$$H_2O + SO_3 + SO_2 + H_2O_2 \rightarrow 2\ H_2SO_4 \quad (1)$$

The solution in the trap tube was put into a flask and added 2-3 drops of brome phenol indicator and then exposed to titration with 0.1 M NaOH solution to determine sulphur contents of apricot samples. The following formula derived from the naturalization reaction between NaOH and H_2SO_4 was used to calculate amount of sulphur in the apricot samples since the neutralization reaction as shown in Equation (2) can take place in the titration process.

$$H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2\ H_2O \quad (2)$$

$$S(ppm) = 16000 \frac{M_{NaOH} V_{NaOH}}{W_{apricot}}$$

Here S stands for amount of sulphur in ppm, M molarity of NaOH solution, V volume of NaOH in L and W weight of apricot sample in kilograms.

3.2 Preparation of apricot samples for vitamins and oil analysis

All slurred apricot samples were centrifuged at 600 rpm for 10 minutes to obtain pellets from the apricot slurry. 2 g of pellets was taken into falcon tube and 10 ml hexane propyl alcohol with butylated hydroxytoluene (BHT) was added into the tube and homogenized in the homogenizer. After homogenization process, the samples were again centrifuged at 600 rpm for 10 minutes and supernatant being formed at the top of tubes was taken and filtered with Whatman No.1 filter paper for analysis of vitamins and oils.

3.2.1 Analysis of vitamins

5 ml methanol-potassium hydroxide was added to the supernatant and the obtained solution was kept in an oven at 85 °C for 20-30 minutes. After the tube was removed from the oven 5 ml distilled water was put into the tube, after that 10 ml hexane propyl alcohol was added and the tube was waited at the room temperature for 12 hours for a phase separation. The supernatant (upper phase) being formed at the top of tube was taken and placed in the oven at 37 °C to evaporate. After evaporation takes place, 1 ml acetonitrile/methanol was added into the tubes with remains of the samples and vortexed and then the samples were taken into 1 ml vials. Analyses were performed by HPCL (Shimadzu, Kyota, Japan) in which acetonitrile/methanol (60 % v +40 % v) was used as a mobile phase at rate of 1 ml/s. The UV detector was used to determine amount of a vitamin. Supelcosil LC18 (14x46 cm, 5 μm, sigma, USA) was used as column. Amounts of vitamin E, D and K were determined with the HPCL according to the method described in the papers by Catignani [21] and Miller, Lorr & Yang [22]. Detection wave length for vitamin E was chosen to be 296 nm and for vitamin D2 and K1 were chosen to be 265 nm.

3.2.2 Analyses of fatty acids

5 ml of 2 % methanolic H_2SO_4 was added into the supernatant obtained from homogenization process and resulting solution was vortexed and incubated at 55 °C for 12 hours. 5 ml of 5 % NaCI was added into the solution after cooling down at the end of the incubation [23]. 5 ml n-hexane was added to methyl ester of fatty acid formed in reaction medium. The levels of all specimens in tubes were made to be equal and they were closed and were made upside-down. After having been waited at room temperature for 5 hours, the supernatant was taken and 5 ml of 2 % $KHCO_3$ solution was added and the sample tubes were closed and made them upside-down and were waited for 3 hours. After this period of time, the supernatant was taken into small tubes exposed in the oven at 37 °C to evaporate. After the evaporation process was completed, the tubes with remains were filled 1 ml n-hexane to solve those remains and then samples were put into vials in which samples were analyzed with Shimadzu GC17. 25 m long, 0.25 μm inner radius, 25 μm film thickness of capillary column (Machery-Nagel, Germany) was used to analyze the sample. During fatty acids analyses, the injection temperature was kept constant at 240 °C and detector temperature at 280 °C and the program for column temperature was adjusted from 120 °C to 220 °C. An increase in the temperature was adjusted to be 5 °C/min. up to 200 °C and after this point, the increase in the temperature was adjusted to be 4 °C/min. up to 220 °C. Nitrogen was used as a carrying gas.

During analysis, methyl ester of standard fatty acid was injected into the GC to determine the time for each fatty acid of a sample analyzed. After performing this operation, the amount of fatty acids was calculated with unit of mg/kg using class GC10 program.

3.2.2.1 Analyses of phytosterol

The determination of phytosterol in oils was carried out according to the method described in ISO 12228-1:2014. In this method, ethanolic potassium hydroxide solution is used to saponify oil by boiling under reflux. The sterols have to be separated from fatty acid anions and the unsaponified mater isolated by solid-phase extraction an

aluminum oxide column (Merck, Darmstadt, Germany). Also the thin-layer chromatography (Merck, Darmstadt, Germany) was used to separate sterols from other unsaponified matters. The separated sterols were determined by GC using betulin as internal standard. 25 m long, 0.25 μm inner radius, 25 μm film thickness of capillary column (Machery-Nagel, Germany) was used to analyze the sample. The conditions applied for temperature here were the same as in fatty acids analysis.

4. Results and Discussion

As mentioned previously, two kinds of fresh apricot samples locally know hacihaliloglu and kabaası were sulphurized in various concentrations of SMBS solution at different immersion times. The Sulphur contents of apricot samples as a function of immersion time for various concentrations of SMBS solution were determined for both kinds of fresh and dried apricot sample. Variations in vitamins and phytosterols of two kinds of fresh apricot samples as a function of immersion time for various concentrations of SMBS solution were also determined.

For each run, the values given in either graphics or tables for the sulphur content, vitamins K1, D2, E and phytosterol and fatty acids were the average value of three apricot specimens that were treated at the same time.

4.1 Variation of sulphur with immersion time

In order to determine the effect of immersion time and concentration of SMBS solution on the sulphur content in apricot samples, two kinds of apricot samples locally known as hacıhaliloglu and kabaası at the same size, the same ripeness, and the same appearance were collected from the same tree for each kind of apricot sample. While some of the samples were put into the sterilized bags and put in refrigerator to use later, some of them were immediately immersed into the SMBS solutions at 5 %, 15 % and 20 % (w/v) for 15, 45, 60 and 90 minutes of immersion times.

The sulfur contents of fresh hacıhaliloglu apricot samples immersed into various concentrations of SMBS solutions as a function of immersion times. It was observed that the sulphur contents of apricot sample increase with increasing immersion time at each concentration of the SMBS solution. The sulphur contents of apricot samples also increase with increasing the concentrations of the SMBS solution. The maximum sulphur content of the apricot samples was obtained at the maximum concentration and the maximum immersion time namely 20 % of the SMBS solution and 90 minutes of immersion time, respectively.

The sulphur content of the fresh kabaaşı apricot samples immersed into 5 %, 15 % and 20 % of SMBS solution as a function of immersion time. As in hacihaliloglu apricot samples, the sulphur contents of kabaası apricot samples increase with increasing immersion times and the concentration of the SMBS solution. While minimum sulphur content of apricot specimens was obtained at the shortest immersion time and the lowest concentration of the SMBS solution, the maximum sulphur content of apricot samples was obtained at the longest immersion time and largest concentration of the SMBS solution. While the sulphur content of hacihalliloglu apricot samples increase with immersion time, those of kabaaşı apricot samples become almost constant after the immersion time of 45 minutes at high concentrations namely 15 % and 20 % of the SMBS solution.

When the sulphur contents of the fresh hacihaliloglu and kabaaşı apricot samples immersed into 5 % of the SMBS solution are compared, it will be seen that the sulphur content of both kinds of apricot samples are close to one another. However, the sulphur contents of the fresh hacıhaliloglu and kabaaşı apricot samples are different from one another at the high concentration namely 15 % and 20 % SMBS solution for all immersion times. Although the amount of sulphur absorbed by both kinds of apricot specimens increase with increasing immersion times, the sulphur contents of kabaaşı apricot samples were found to be higher than those of hacıhaliloglu for all immersion times at high concentrations namely 15 % and 20 % SMBM solutions. While sulphur content of hacihaliloglu apricot samples increase linearly with immersion time at all concentrations of the SMBS solution, those of kabaaşı apricot samples became almost constant after the immersion time of 45 minutes at high concentration namely 15 % and 20% of the SMBS solutions.

4.2 Effect of drying on sulphur content of apricot samples

Two kinds of apricot samples locally known as hacıhaliloglu and kabaaşı sulphurized in the 5, 15 and 20 % SMBS solutions for the immersion times of 15, 45, 60 and 90 minutes were dried in open air for seven days. The variation of sulphur content in the dried apricot samples as a function of immersion times and the concentrations of the SMBS solution were also determined for hacihaliloglu and kabaası apricot samples. As expected, the trend for sulphur content obtained during sulphurization was observed to be maintained after drying process. In other words, the apricot samples with the highest or the lowest sulphur content in the sulphurization had the highest or the

lowest sulphur content after drying, respectively. While the sulphur contents of the fresh hacihaliloglu and kabaaşı apricot samples sulphurized in 5 % of SMBS solution were close to one another for all immersion times, the sulphur contents of the dried hacihaliloglu and kabaaşı apricot samples were found to be different from one another for all immersion times. Before drying, the sulphur contents of hacihaliloglu apricot samples were less than those of kabaaşı apricot samples for concentrations higher than 5 % SMBS solution. After drying, the trend for sulphur content of apricot samples was maintained. The existed difference between the sulphur contents of the hacihaliloglu apricot samples and that of the kabaaşı apricot samples increased with drying. This can be attributed to the structure of kabaası apricot samples allows water to evaporate more than that of hacihaliloglu. The levels of moisture, carbohydrate, cellulose, nutrient, mineral contents, calorific values, vitamins depend on variety of apricot. Therefore, the apricot variety is an important parameter and some kinds of apricots are more appropriate for drying to give high vitamins, mineral-rich products and calorific values [10]. Amounts of moisture, carbohydrate, protein, oil, total acid, cellulose and ash in apricots change with apricot varieties [9].

Amount of sulphur per unit mass of the apricot samples increases according to evaporation of water in the structure of apricot samples with drying time.

4.3 Effect of sulphur content on vitamin and phytosterol of apricot samples

Vitamin K1, vitamin D_2, and vitamin E (α tocopherol and σ tocopherol) were found in all apricot samples considered in the present study. The amount of α tocopherol in the apricot samples was found to be higher than those of other vitamins. Amount of vitamin K1 of the fresh hacihaliloglu apricot samples sulphurized in 5, 15 and 20 % SMBS solutions was illustrated in Figure 1*a* as a function of immersion times. As can be seen from the figure amount of vitamin K1 in the fresh hacihaliloglu apricot samples decreases with increasing both the concentrations of the SMBS solution and the immersion times, and thus, the content of sulphur in the specimen. While the highest value for vitamin K1 was obtained at the lowest concentration of the SMBS solution and the shortest immersion time, the lowest value for vitamin K1 was obtained at the highest concentration of the SMBS solution and the longest immersion time.

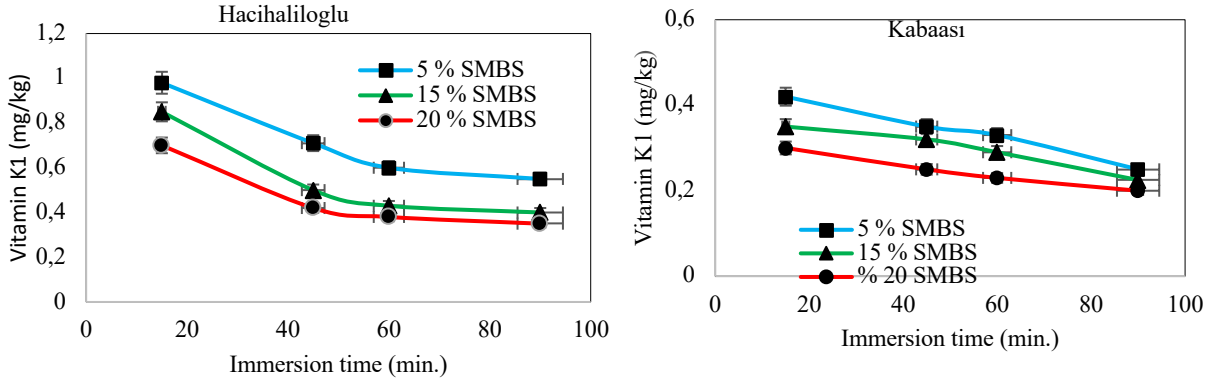

Figure 1. Variation of vitamin K1 of fresh apricot samples with immersion times for various concentrations of SMBS solution
(a: Hacihaliloglu, b: Kabaası)

The trend for variation of vitamin K1 with the concentration of SMBS solution and the immersion time similar to hacihaliloglu apricot samples was observed for kabaaşı apricot samples as illustrated in Figure 1b. While the highest value for vitamin K1 was obtained at the lowest concentration of the SMBS solution and the shortest immersion time, the lowest value for vitamin K1 in the fresh kabaaşı apricot samples was obtained at the highest concentration of the SMBS solution and the longest immersion time.

Vitamin K1, resisting heat, dissolvable in oil, can be inactivated by alkali strong acids, radiation and oxidase agents. Here while acidity of apricot samples increases with sulphur content, the concentration of SMBS solution and the immersion time makes the amount of vitamin K1 decrease in the apricot samples.

Variation of σ tocopherol in hacihaliloglu apricot samples with concentration of the SMBS solutions and immersion times were depicted in Figure 2a. As can be seen in the figure while the highest value for σ tocopherol

in the fresh apricot samples sulphurized in various concentrations and immersion times was found at the lowest concentration and the shortest immersion time, the lowest σ tocopherol in the fresh apricot sample was obtained at the highest concentration of SMBS solution and the longest immersion time. The trend for variation of σ tocopherol with concentration of the SMBS solution and immersion time similar to hacihaliloglu was observed for kabaaşı apricot samples as evidenced in Figure 2b

Variation of vitamin D_2 in the fresh hacihaliloglu apricot samples sulphurized in 5, 15 and 20 % SMBS solution was illustrated in Figure 3a as functions of immersion times of 15, 45, 60 and 90 minutes. As seen in the figure while the highest value for vitamin D_2 in the fresh apricot samples sulphurized in various concentrations and immersion times was found at the lowest concentration of SMBS solution and the shortest immersion time, the lowest vitamin D_2 in the fresh apricot sample was obtained at the highest concentration of SMBS solution and the largest immersion time. The trend for variation of vitamin D_2 with concentration of the SMBS solution and immersion time similar to hacihaliloglu apricot specimens was observed for kabaaşı apricot samples as evidenced in Figure 3b.

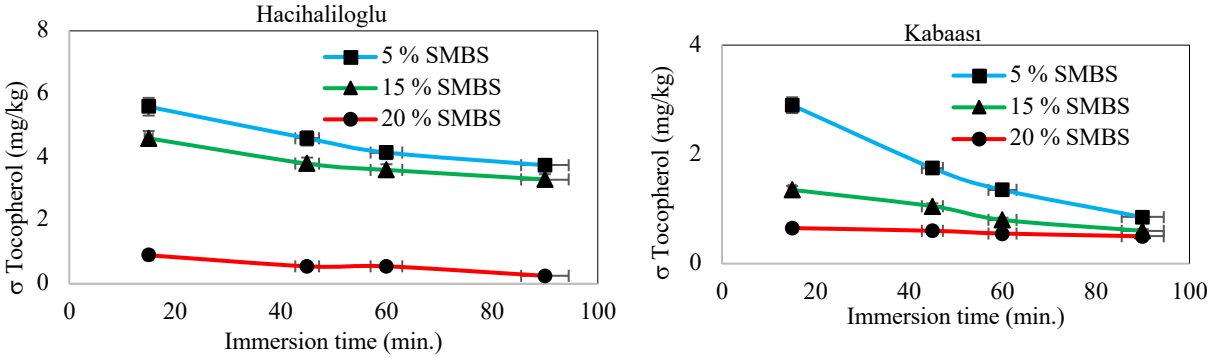

Figure 2. Variation of σ-tocopherol of fresh apricot samples with immersion times for various concentrations of SMBS solution
(a: Hacihaliloglu, b: Kabaası)

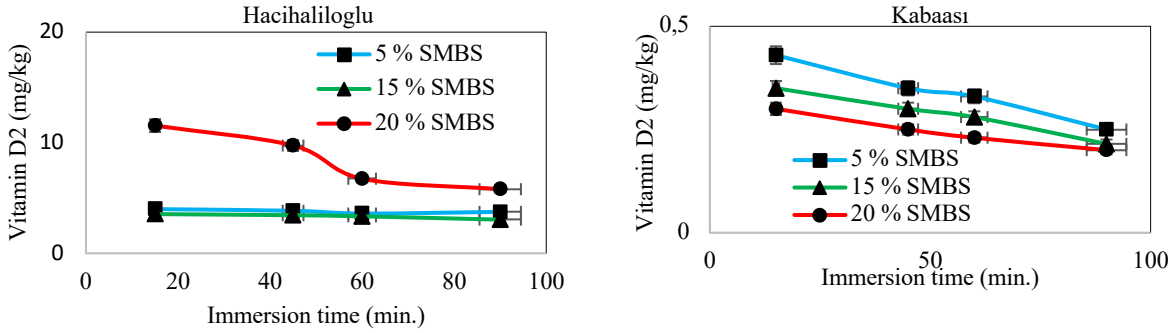

Figure 3. Variation of vitamin D2 of fresh apricot samples with immersion times for various concentrations of SMBS solution
(a: Hacihaliloglu, b: Kabaası)

The α tocopherol (vitamin E) that is a quite powerful antioxidant decreased with increasing concentration of SMBS solution and immersion times for both sulphurized fresh hacihaliloglu and kabaaşı apricot samples. In other words, while the highest value of α tocopherol in both sulphurized fresh hacihaliloglu and kabaaşı apricot samples was observed at the lowest concentration and the shortest immersion time, the lowest value of α tocopherol in both sulphurized fresh hacihaliloglu and kabaaşı apricot samples was found at the highest concentration of SMBS solution and the longest immersion times as illustrated in Figure 4a and Figure 4b, respectively.

It is known that vitamins can be oxidized with time, heat and light. Amounts of vitamins decreased with increasing concentrations of SMBS solution and prolonging immersion times as evinced in Figs. 1-4. In this study, the enzyme causing oxidation may be inhibited with acidification in some apricot samples (pH less than 4.2). As

mentioned earlier, Jiang et al. [24] reported that no polyphenol oxidase activity was observed in the enzymatic reaction below pH 4.2. Moreover, it was indicated that co-pigmentation of anthocyanins in litchi fruit can be formed with a suitable treatment with acids and thus, stabilized the anthocyanin pigments [25].

Processing time, temperature, oxygen concentration in drying atmosphere, light, and pH value of a sample affect the loss of vitamins during fruit and vegetable processing. As can be seen from Figs. 1-4, amounts of vitamins of K1, D2 and E in both kinds of apricot samples sulphurized in various concentrations of SMBS solution at different immersion times decreased with increasing concentrations of SMBS solution and prolonging immersion times. This observation agrees with previous studies ([27], [4], [26], [28]). Karabulut et al. [26] reported that the light accelerated degradation in vitamin C. Furthermore, it was reported that degradation in vitamin C can be accelerated with light intensity and an increase in Sulphur content of samples ([28] and [4]).

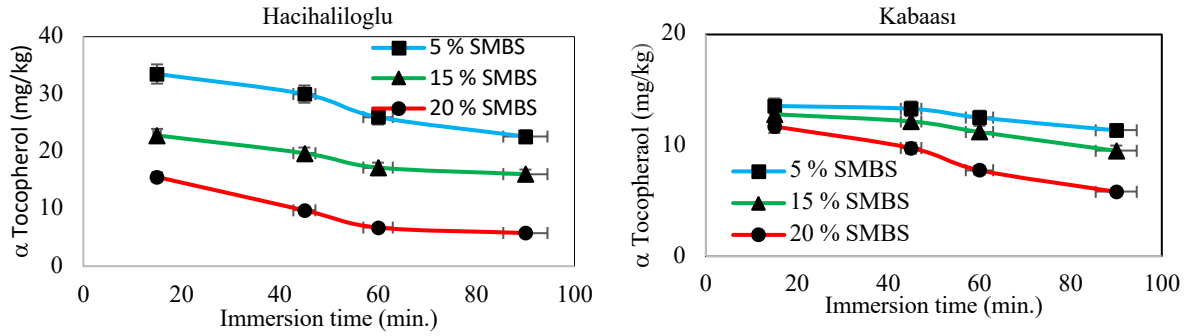

Figure 4. Variation of α-tocopherol of fresh apricot samples with immersion times for various concentrations of SMBS solution
(a: Hacihaliloglu, b: Kabaası)

The ergosterol, sigmasterol and β-sitosterol were found in both hacihalliloglu and kabaaşı apricot samples. The stigmasterol among the phytosterols was observed to be the largest one in the hacihalliloglu apricot samples. Amounts with standard deviations of the β-sitosterol, the stigmasterol and ergosterol in the fresh hacihaliloglu and kabaaşı apricot samples sulphurized in various concentrations of the SMBS solutions at different immersion times are given in Table 1 and Table 2, respectively. As can be seen in the tables the relation between amount of ergosterol and sulphur content in the samples is not in order. Amount of ergosterol in the fresh hacihaliloglu apricot samples sulphurized in 5 and 15 % of the SMBS solution are higher than those in the fresh kabaaşı apricot samples sulphurized in the same concentration of SMBS solution.

The relationship between concentrations of SMBS solution and thus, sulphur content and the stigmasterol content in both kinds of apricot samples are not in order as seen in Table 1 and Table 2. The stigmasterol in both kinds of apricot samples are usually higher than that of the ergosterol. As being the ergosterol and the stigmasterol, β-sitosterol contents in both kinds of apricot samples do not change orderly with concentrations of the SMBS solution and immersion times as illustrated in Table 1 and Table 2, respectively.

While the myristic acid, palmitic acid (16:0), linoleic acid (18:2, n6t) and α-linoleic acid (18:3, n3) were found to be in all apricot samples considered in present study, the other types of fatty acids were encountered some of the apricot samples. The contents of palmitic acid of fresh hacihaliloglu and kabaaşı apricot samples sulphurized in various concentrations of SMBS solution at different immersion times were found to be 91 mg/kg and 110 mg/kg, respectively. The given value of palmitic acid for each kind of apricot sample was an average of lots of apricot samples sulphurized in various concentrations of SMBS solution at different immersion times.

The contents of myristic acid of fresh hacıhaliloglu and kabaaşı apricot samples sulphurized in various concentrations of SMBS solution at different immersion times were found to be 198.1 mg/kg and 121.1 mg/kg, respectively. The given value of myristic acid for each kind of apricot sample was an average of a lot of apricot samples sulphurized in various concentrations of SMBS solution at different immersion times.

Table 1. Values of phytosterols for hacihaliloglu apricot samples

Immersion time (min.)	Concentration of SMBS solution								
	5 %	15 %	20 %	5 %	15 %	20 %	5 %	15 %	20 %
	β-sitosterol (mg/kg)			Stigmasterol (mg/kg)			Ergosterol (mg/kg)		
15	48,75 ±4.2	77 ±6.5	42 ±3.35	88,6 ±6.34	95,7 ±8.2	54,2 ±5.16	1,7 ±0.165	6,7 ±0.93	1,95 ±0.113
45	39,2 ±3.43	63 ±5.23	42,5 ±3.85	99,9 ±8.35	90,6 ±7.2	0,1 ±0.012	1,5 ±0.132	4,6 ±0.82	0,95 ±0.054
60	26,15 ±2.3	85,05 ±6.4	85,85 ±8.2	111,05 ±10.52	92,15 ±8.5	ND ±0	1,4 ±0.135	2,25 ±0.213	1,7 ±0.144
90	68,6 ±5.25	92,15 ±7.3	53,2 ±4.87	157,6 ±13.65	90,3 ±7.6	0,35 ±0.028	3,51 ±0.292	1,5 ±0.145	0,45 ±0.075

The numbers after ± sign point out standard deviation. ND: not detected

Table 2. Values of phytosterols for kabaasi apricot samples

Immersion time (min.)	Concentration of SMBS solution								
	5 %	15 %	20 %	5 %	15 %	20 %	5 %	15 %	20 %
	β-sitosterol (mg/kg)			Stigmasterol (mg/kg)			Ergosterol (mg/kg)		
15	84,8 ±6.2	35,65 ±3.25	49,45 ±4.85	98,6 ±7.62	87,2 ±7.65	89,1 ±8.65	0,25 ±0.025	0,05 ±0.0042	2,6 ±0.18
45	75,3 ±6.54	33,1 ±2.83	53,05 ±5.25	66 ±6.35	89,8 ±7.85	98,8 9.35	ND ±0	0,075 ±0.0035	3,2 ±0.22
60	29,6 3.15	26,2 ±2.03	39,45 ±4.35	56,8 ±4.85	88,25 ±8.38	67,7 ±5.78	0,1 ±0.015	0,125 ±0.021	23 ±2.43
90	94,2 ±8.5	39,55 ±3.52	11,8 ±1.15	107 ±9.82	84,85 ±7.85	41,6 ±3.83	0,95 ±0.097	0,145 ±0.0135	1,2 ±0.097

The numbers after ± sign indicate standard deviation. ND: not detected

While the average values of linoleic acid (18:2, n6t) and α-linoleic acid (18:3, n3) of fresh hacihaliloglu apricot samples sulphurized in various concentrations of SMBS solution at different immersion times were found to be 121.5 mg/kg and 77.3 mg/kg, respectively, the average values of those acid in kabaaşı apricot samples sulphurized at the conditions that were applied to hacihaliloglu apricot samples were found to be 63 mg/kg and 64.3 mg/kg, respectively.

The acids such as palmitoleic acid (16:1, n7), stearic acid (18:0), oleic acid (18:1, n9t), oleic acid (18:1, n9c), linoleic acid (18:2, n6c) and arachidonic acid (20:4, n6) were encountered in some samples.

5. Conclusions

Two kinds of apricot samples locally known hacihaliloglu and kabaaşı were sulphurized in various concentrations of SMBS solution at different immersion times. The sulphur contents of fresh apricot samples as a function of immersion time were depicted for each kind of apricot samples for various concentrations of SMBS solution. Furthermore, the sulphur contents of the apricot samples dried open air for a week were determined as a function of immersion time for each kind of apricot samples for various concentrations of SMBS solution. Variations of vitamins of K1, D2 and E and phytosterols in each fresh apricot sample were determined as a function of immersion time for various concentrations of SMBS solutions and thus, the sulphur contents of apricot samples. It was observed that amount of vitamins of K1, D2 and E decreased with increasing concentration of SMBS solution and prolonging immersion time and thus, increasing sulphur content of both kinds of apricot samples. Variations of phytosterol in both kinds of apricot samples sulphurized in various concentration of SMBS solution at different immersion times were not in order. While fatty acids such as the myristic acid, palmitic acid and oleic acid were determined in all apricot samples sulphurized in various concentrations of SMBS solution at different immersion times, the palmitoleic acid, stearic acid, oleic acid and arachidonic acid were encountered in some samples.

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