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Effect of sulphuring on physicochemical characteristics and aroma of dried Alkaya apricot: a new Turkish variety

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Abstract: Sulphured and unsulphured sun-dried apricots of Alkaya, a new variety of *Prunus armeniaca* L. grown in the Malatya region of Turkey, were compared to study the effects of sulphur treatment on their physicochemical characteristics and aroma compounds. Colour, texture, moisture, pH, total soluble solids, sugars, organic acids, and 5-hydroxymethyl furfural contents were determined. Aroma compounds were quantified and identified by GC–MS-FID. Sulphuring treatment before sun-drying had significant effects on some physicochemical properties (pH, titratable acidity, total acids, and colour parameters) and aroma compounds of Alkaya apricots. Colour parameters showed that browning was higher in the unsulphured apricots than in the sulphured ones. A total of 45 aroma compounds were identified. Sulphuring treatment significantly affected the aroma compound profile of the dried apricots. In general, the levels of aroma compounds in sulphured apricots were found to be significantly lower than those in the unsulphured ones ($P < 0.05$). Pyrazines were detected only in the unsulphured apricots. The significantly higher level of norisoprenoids, lactones, esters, pyrazines, and furfural in the unsulphured dried apricots was attributed to degradation of carotenoids, oxidation of long-chain fatty acids, thermal degradation, and Maillard reaction.

Key words: Alkaya, dried apricots, sulphuring, colour, aroma compounds

1. Introduction

Drying is one of the oldest preservation techniques for foods and is the most important process in the successful storage of apricots (Göğüş et al., 2007). The objective in drying apricots is to reduce the moisture content to a level that allows safe storage over an extended period. In Turkey, the most common drying method for apricots is open-air sun-drying, requiring low capital, simple equipment, and low energy input (El Halouat and Labuza, 1987; Gezer et al., 2003). Generally, the fruits are spread on rooftops or on rocks without subjecting them to any pretreatment or washing with water (Mir et al., 2009). To decrease the effect of spoilage reactions, to facilitate the drying process, to prevent browning, to ensure colour stability, and to improve the overall product quality, some pretreatments are advised. One of these treatments is sulphuring (Rossellò et al., 1993; Lewicki, 2006; Miranda et al., 2009). Sulphur dioxide is used widely in the food industry to prevent quality losses of foods and to reduce fruit darkening rate during drying and storage. Both enzymatic and nonenzymatic browning and microbial activity are prevented by using sulphites at low concentration (Joslyn and Braverman, 1954). The oxygen-scavenging action of sulphur dioxide helps in stabilising the carotenes. When sulphur dioxide is absorbed into the fruit, it is converted mainly to the bisulphate ion, which remains free and retards the formation of Maillard-type compounds, and it can also be reversibly bound to certain compounds, such as the carbonyl group of aldehydes. This bound sulphite is considered to have no retarding effect on product deterioration (Bolin and Jackson, 1985; Mir et al., 2009).

It was reported that sulphites cause some health problems such as asthmatic reactions when inhaled or ingested by sensitive individuals (Freedman, 1980; Miranda et al., 2009). Alternatively, unsulphured sun-dried (natural) apricots have been produced in Turkey. These apricots have a dark-brown colour and no noticeable sulphur taste, which has attracted consumers' attention in recent years (Karabulut et al., 2007).

According to the FAO Statistical Database (http://faostat.fao.org), the world production of apricots is 4,111,076 t. Producing about 20% of the apricots in

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the world (811,609 t), Turkey is the leading producer (http://faostat.fao.org) and provides about 75% of the world's dried apricots. Despite wide cultivation in many parts of the world, it was reported that the favourable climatic and geographical factors in the Malatya region of eastern Turkey enable the production of apricots that are well known and appreciated by consumers for their characteristic high dry matter, sugar content (Akin et al., 2008), and aroma (Botondi et al., 2003; Munzuroglu et al., 2003). More than 50% of the fresh apricots and 90%–95% of the dried apricots of the whole country are produced in this region and about 80% of world dried apricot exports come from this region (Asma, 2000; Munzuroglu et al., 2003; Karabulut et al., 2007; Gokbulut and Karabulut, 2012). The most commonly cultivated apricot varieties in the Malatya region are the Hacıhaliloğlu, Çataloğlu, Kabaaşı, Soğancı, Çoloğlu, Soğanoğlu, Hasanbey, and Zerdali types (Asma, 2000). These typical varieties are protected by the Turkish Patent Institute as geographical indications in Turkey (http://www.turkpatent.gov.tr). Hacıhaliloğlu, Çataloğlu, Kabaaşı, Soğancı, and Çologlu, cultivars are evaluated as dry products while the others are consumed as fresh fruit (Hacıseferoğulları et al., 2007; Akin et al., 2008; Gokbulut and Karabulut, 2012). A considerable amount of the annual production of apricots in the Malatya region is dried after sulphuration (Akin et al., 2008). Recently, a new dried table apricot cultivar, Alkaya, cultivated in Malatya Province has attracted the attention of researchers for its very good pomological characteristics (Yilmaz et al., 2010).

Many studies have reported on the technological and nutritional properties of apricots cultivated in the Malatya region (Munzuroglu et al., 2003; Hacıseferoğulları et al., 2007; Akin et al., 2008). Numerous investigations have been carried out on fresh and dried forms and on their carbohydrate, amino acid, mineral, and vitamin contents (Belloso and Barriobero, 2001; Munzuroglu et al., 2003). There are a few studies on the volatile compounds of fresh apricots (Chairote et al., 1981; Takeoka et al., 1990; Guillot et al., 2006) and apricot juice (Riu-Aumatell et al., 2004). However, there has been no detailed research on the volatile compounds of dried apricots.

Therefore, the present investigation evaluated the effects of sulphuring on physicochemical characteristics, sugars, and aroma compounds of dried apricots from the Malatya region of Turkey of the new variety Alkaya that, to our best knowledge, has been scarcely studied.

2. Materials and methods

2.1. Materials

About 2000 kg of apricots of the Alkaya variety from the Malatya region (Turkey) were considered. Fruits of proper maturity, uniform size, colour, and texture were collected from the experimental orchards of the Malatya Apricot Research Station. The ripeness was determined according to total soluble solids (TSS%), titratable acidity (TA%), pH, size, colour, and texture. In ripe apricots, TSS, TA, and pH were 19.5%, 0.3%, and 4.9, respectively. The apricots were picked and divided into two different lots. Afterwards, the apricots of each lot were halved, pitted, and then submitted to drying (unsulphured samples) or sulphuring and drying (sulphured samples) processes. The sulphuring process was carried out by burning elemental sulphur in a special airtight reinforced concrete chamber (13 m^3, 2.5 m width × 2.5 m length × 2.2 m height). Fresh apricots were loaded onto trays (in a single layer) that were placed in the racks of the trolleys. Two kilograms of elemental sulphur was burned in the chamber for 8 h for 1000 kg of fresh apricots. After treatment with sulphur, fruits were dried under the sun for 8 days until the moisture content was reduced to 20%. Unsulphured apricots were placed on the trays and dried directly under the sun for 9 days until moisture content was reduced to 20%. The measured temperatures during drying were 34–40 °C in daylight and 18–22 °C at night. Dried apricots were placed into polyethylene bags and stored at 4 °C and 50% relative humidity until the analysis. All the results reported in the tables are thus the mean values of the data obtained from each lot.

2.2. Chemicals

All the reagents and solvents used were obtained from J.T.Baker (Deventer, the Netherlands) and Merck (Darmstadt, Germany). Standard compounds were purchased from Sigma-Aldrich Chemical Company (St. Louis, MO, USA).

2.3. Physicochemical analyses

The moisture content of dried apricots was determined according to the AOAC official methods (AOAC, 1990). Titratable acidity, pH, and soluble solids content were determined as follows. Both apricot samples (10 g each) were homogenised with 40 mL of distilled water to obtain a purée. Titratable acidity was determined by diluting 5 g of the homogenised apricots with 50 mL of deionised water and titrating to pH 8.1 with 0.1 N NaOH using a pH-meter (MP 220 Mettler Toledo, Greifensee, Switzerland). The results were expressed as the percentage of malic acid. The pH was measured with the same equipment used for titratable acidity, while the soluble solids content was determined from the purée with a refractometer (2WAJ ABBE bench refractometer, Optika Microscopes, Bergamo, Italy) and expressed as °Brix. Texture analysis was performed by measuring the maximum shear force using a texture analyser (TR 53205, Forlì, Italy) fitted with a stainless steel probe of 1/4 cm in diameter and a length of 5 cm. Firmness was reported as the force in newtons needed to penetrate 10 mm of dried apricot. Each sample comprised 10 fruits; each fruit was read at 4 points both

on the lower and upper surface. Data were recorded in duplicate. Colour values were measured from the surface (skin) and in the flesh of the dried apricot with a handheld colorimeter (NR-3000, Nippon Denshoku Ind. Co. Ltd., Tokyo, Japan) using D65 illuminant at a 10° observer angle. The CIE colour parameters L^* (lightness), C^* (chroma), $h°$ (hue angle), a^*, and b^* were measured. Four readings were collected for each sample (ten sulphured and ten unsulphured fruits).

2.4. 5-Hydroxymethyl furfural (HMF) analysis

For each homogenised sample (both sulphured and unsulphured), obtained as described above, 6 g of homogenate was centrifuged at 5000 rpm for 30 min at 4 °C. The supernatant was filtered through a 0.45-μm filter (Albet, Barcelona, Spain) and immediately injected into an HPLC instrument (Shimadzu USA Manufacturing Company Inc., Class VP LC-10ADvp) equipped with a diode array detector (Shimadzu SPD-M10Avp) and a Varian Omnisphere C18 column (150 mm × 4.6 mm, 5 μm) fitted with a guard cartridge packed with the same stationary phase. HPLC conditions were set according to Arena et al. (2011a). Three analyses were performed for each sample.

2.5. Sample preparation and extraction of sugars and organic acids

For each homogenised sample (both sulphured and unsulphured), 1 g of homogenate was mixed with 5 mL of absolute ethanol and heated in a water bath for 15 min at 50 °C. Afterwards the solvent was evaporated under reduced pressure using a Rotavapor (RE 111, Büchi, Switzerland), and then 2 mL of stock solution (0.25 g hydroxylamine + 0.06 g phenyl-β-D-glucopyranoside (internal standard)/10 mL pyridine) was added. The resulting solution was heated for 30 min at 75 °C and then 1 mL of hexamethyldisilazane and 0.1 mL of trifluoroacetic acid were added. The solution was stirred for 30 s and allowed to stand for 30 min. The supernatant was recovered and 1 µL was injected into the GC-FID apparatus. Sugars and organic acids were determined as their trimethylsilyl-oxime ether/ester derivatives (Serra and Ventura, 1993). Three analyses were performed for each sample.

2.6. GC-FID conditions

A gas chromatograph, Shimadzu GC-2014, equipped with a flame ionisation detector (FID) was used to analyse both sugars and organic acids. The operating conditions were as follows: a CP-Wax 52 CB capillary column (Chrompack, 30 m, 0.25 mm inner diameter, 0.25 µm film thickness). Helium was used as the carrier gas with a constant column flow rate of 1 mL/min; split ratio was 20:1; the oven temperature was kept at 50 °C for 1 min, from 50 °C to 120 °C at 10 °C/min, from 120 °C to 200 °C at 2 °C/min, from 200 °C to 280 °C at 10 °C/min, and then held for 30 min at 280 °C. Sugars and organic acids were identified by comparing retention times to those of standards. Each compound was quantified based on its peak area relative to that of the internal standard.

2.7. Sample preparation and extraction of aroma compounds

For each homogenised sample 50 g of homogenate was mixed with 40 mL of pentane and dichloromethane (2:1, v/v) and 100 µL of 4-nonanol (40 µg/100 mL) as an internal standard. Then the mixture was stirred at 9000 rpm for 15 min at 4 °C. The organic phase was recovered and concentrated to a volume of 1 mL with a Vigreux distillation column (Selli et al., 2006). Finally, the extract was injected into the GC-FID and GC-MS apparatus. Three analyses were performed for each sample.

2.8. GC-FID and GC-MS conditions

GC-FID analysis of aroma compounds was performed using an Agilent 6890 chromatograph equipped with a DB-Wax column (J&W Scientific, 30 m, 0.25 mm inner diameter, 0.25 µm film thickness) and a FID. Helium was used as the carrier gas with a constant column flow rate of 1.5 mL/min; the injection volume was 2 µL; the oven temperature was kept at 40 °C for 4 min, from 40 °C to 220 °C at 2 °C/min, from 220 °C to 245 °C at 3 °C/min, and then held for 20 min at 245 °C. The injector and FID detector were kept at 250 °C during analysis. Identification of the compounds was performed by GC-MS. An Agilent 5975B mass spectrometer with a mass selective detector fitted with the same DB-Wax column and operated in the same conditions used for GC analysis was coupled to the GC. Helium was used as the carrier gas with a constant column flow rate of 1.5 mL/min. Injection volume was 2 µL. The transfer line temperature was 250 °C. The mass detector was operated in electron impact mode at 70 eV in a range of 29–350 amu at 2-s intervals. Identification of the compounds was performed by comparing the linear retention index and electronic mass spectra with reference compounds or published data and mass spectra libraries. The retention indices of each compound were calculated by using *n*-alkane series from C8 to C32 injected under the same conditions. Each compound was quantified based on its peak area relative to that of the internal standard.

2.9. Statistical analysis

The results were compared by one-way analysis of variance (ANOVA) using StatGraphics Plus 4.1 software (Manugistics Inc., Rockville, MD, USA). Duncan's multiple range tests were used to compare the significant differences of the mean values reported in Tables 1–3, and the statistical significance of the differences between samples was determined using the F-test. The level of statistical significance was $P < 0.05$ at the 95% confidence level.

3. Results and discussion

3.1. Physicochemical characteristics

The physicochemical characteristics of sulphured and unsulphured Alkaya dried apricots are reported in Table 1. The drying time for unsulphured apricots was reported to be greater than that for sulphured apricots (Karabulut et al., 2007), and sulphuring is also used to enhance and to facilitate the drying process (Rossellò et al., 1994; Miranda et al., 2009). As shown in Table 1, sulphured apricots had a similar ($P > 0.05$) average moisture content (22.5%) to that of unsulphured apricots (22.1%). Both average pH value and average titratable acidity value of sulphured apricots were significantly different from the unsulphured apricots ($P < 0.05$). The high pH values of dried apricots, both sulphured and unsulphured, could be ascribed to the quality parameters of fresh apricots and it was determined that all Malatya apricot varieties have considerably higher pH values as compared to the values reported in the literature (Akin et al., 2008). Sulphuring treatment significantly ($P < 0.05$) increased the average acidity (% malic acid) of sulphured samples compared with the unsulphured ones. The average soluble solids contents (°Brix) were not statistically different ($P > 0.05$) between sulphured (68.0) and unsulphured (66.8) samples. Average values for firmness (N) were similar ($P > 0.05$) for both sulphured (4.0) and unsulphured (4.1) dried apricots, indicating that sulphuring did not influence the firmness of the dried fruits.

Colour values of sulphured and unsulphured Alkaya dried apricots (skin and flesh) are shown in Table 1. The CIE colour parameters have been widely used to describe colour changes during thermal processing of fruit and vegetable products. The colour variables have been related to the types and quantities of some components present in fruits and vegetables (Ameny and Wilson, 1997; Sass-Kiss et al., 2005) and the moisture content of fresh and dried apricots (Karabulut et al., 2007; Özkan et al., 2003).

The average L^*, C^*, and $h°$ values for both skin and flesh (except C^* in skin) of the unsulphured dried apricots were significantly lower ($P < 0.05$) in comparison with sulphured apricots. This suggests that the severity of the browning process, due both to nonenzymatic and enzymatic browning, was higher in unsulphured apricots with respect to the sulphured ones. It was reported that sulphured apricots have higher CIE values than unsulphured apricots or those with low sulphur dioxide content (Rossellò et al., 1994; Karabulut et al., 2007). The average L^* (lightness) values of sulphured apricots (66.5 and 78.7 for skin and flesh, respectively) were significantly ($P < 0.05$) higher than those of unsulphured apricots (22.6 and 18.8 for skin and flesh, respectively), confirming the darkening of the colour without sulphuring pretreatment. The C^* (chroma) values, which represent colour saturation, in general increased with sulphuring treatment of dried apricots (Karabulut et al., 2007). In our samples the average C^* value increased significantly ($P < 0.05$) with sulphuring only in the flesh (27.7 and 10.7 for sulphured and unsulphured dried

Table 1. Physicochemical characteristics of sulphured and unsulphured Alkaya dried apricots.

Moisture (%)	Sulphured		Unsulphured		P
	22.5 (1.62)[β]		22.1 (1.29)		
pH	4.5 (0.07)		5.1 (0.05)		*
Titratable acidity (% malic acid)	1.8 (0.02)		1.3 (0.03)		*
Soluble solids (°Brix)	68.0 (0.08)		66.8 (0.10)		
Firmness (N)	4.0 (0.34)		4.1 (0.24)		
Colour parameters	Skin	Flesh	Skin	Flesh	
L^*	66.5 (3.70) b	78.7 (11.3) b	22.6 (6.99) a	18.8 (7.19) a	*
C	25.7 (2.84) a	27.7 (2.73) b	28.0 (3.54) a	10.7 (3.78) a	*
h	78.5 (0.99) b	77.8 (3.53) b	9.1 (7.48) a	24.9 (3.82) a	*
a^*	5.12 (1.92) a	5.7 (2.17) a	27.6 (1.67) b	9.8 (1.45) b	*
b^*	25.1 (2.05) b	27.0 (3.51) b	4.5 (1.67) a	3.8 (1.84) a	*

[β]Standard deviation in parentheses.

*Mean values are statistically different ($P < 0.05$). Mean values with different letters (a, b) within the same row are statistically different ($P < 0.05$).

apricots, respectively). This increase was not observed in the skin (25.7 and 28.0 for sulphured and unsulphured dried apricots, respectively). The average C^* value of the flesh of sulphured dried apricots was higher than that of the skin; the opposite was observed for unsulphured dried apricots. An increase of $h°$ value was observed with the sulphuring process. The same trend was observed by Karabulut et al. (2007) in apricots of a different variety. The increase of a^* values and the severity of the decrease of the b^* values both in the skin and flesh of unsulphured apricots shows the darkening of the colour.

3.2. HMF content

HMF is a well-known indicator of heat processing and/or storage of several food products (Arena et al., 2001; Rada-Mendoza et al., 2002; Delgado-Andrade et al., 2009) and dehydrated foodstuffs such as fruits (Sanz et al., 2001; Komes et al., 2005). The presence of HMF was not detected in sulphured or unsulphured dried apricot samples, but this cannot exclude browning due to the Maillard reaction. In fact, the pH value of dried apricots, 4.5 and 5.1, respectively, is not favourable to HMF accumulation (Fallico et al., 2008). However, it could lead to the accumulation of other intermediates of the Maillard reaction, such as dicarbonyl compounds (Arena et al., 2011a, 2011b).

3.3. Sugars and organic acids

The main sugars, both in sulphured and unsulphured dried Alkaya apricots, were sucrose, glucose, sorbitol, and fructose (Table 2), accounting for more than the 98% of the total sugars and ranging individually from 31% to 16%. Sucrose, although being the major sugar in all samples, probably due to hydrolysis, was lower in the sulphured samples than in the unsulphured ones. In fact, both glucose and fructose were higher in the sulphured dried apricots than in the unsulphured ones (Table 2).

Sulphuring did not influence the sorbitol content. Its level was considerably higher than in apricots grown in other countries (Forni et al., 1997; Dolenc-Sturm et al., 1999; Katona et al., 1999), reaching about 23 g/100 g dry matter (Table 2), confirming this to be a characteristic of Malatya apricots (Akin et al., 2008). It is reported that sugar alcohol sorbitol is more beneficial than other sugars with regard to dental health and diet control, because the

Table 2. Concentration (g/100 g dry matter) of sugars and organic acids identified in sulphured and unsulphured Alkaya dried apricots.

Sugars	Sulphured	Unsulphured	P
Sucrose	23.8 (1.37)[a]	27.6 (1.13)	*
Glucose	23.5 (1.43)	21.3 (2.15)	*
Sorbitol	22.6 (2.23)	23.0 (3.14)	
Fructose	16.4 (1.66)	13.8 (1.76)	*
Xylose	0.5 (0.50)	-	
myo-Inositol	0.5 (0.18)	0.3 (0.20)	*
Galactose	0.3 (0.24)	0.2 (0.08)	*
Mannitol	0.2 (0.12)	-	
Raffinose	0.1 (0.09)	0.1 (0.08)	
Mannose	-	0.2 (0.10)	*
Total sugars	87.9 (1.17)	86.5 (1.48)	
Organic acids			
Malic	1.2 (0.57)	1.1 (0.72)	*
Quinic	0.5 (0.44)	0.3 (0.23)	
Citric	0.4 (0.22)	0.4 (0.25)	
Total acids	2.1 (0.04)	1.8 (0.04)	*

*Mean values are statistically different ($P < 0.05$). Mean values with different letters (a, b) within the same row are statistically different ($P < 0.05$).
[a]Standard deviation in parentheses.

different metabolism of sorbitol in comparison to other sugars results in lower energetic input to the body, and it improves the taste and texture of fruits (Akin et al., 2008). Moreover, polyols like sorbitol and mannitol were used to sweeten food for diabetics (Dolenc-Sturm et al., 1999).

Xylose and mannitol were detected only in sulphured dried apricots (Table 2). The average content of xylose (0.5 g/100 g DM) was similar to that reported for Slovenian apricots (Dolenc-Sturm et al., 1999).

myo-Inositol and galactose were the highest in sulphured samples, while mannose was the highest in the unsulphured dried apricots. Raffinose was detected in low amounts in both samples (Table 2).

The organic acids content of sulphured and unsulphured dried Alkaya apricots is shown in Table 2. Malic acid was the predominant organic acid and was the highest in the sulphured dried apricots. The amounts of quinic and citric acids were similar in both samples (Table 2).

3.4. Aroma compounds

The mean levels of aroma compounds of the sulphured and unsulphured dried Alkaya apricots and their linear retention indices on the DB-Wax column are shown in Table 3. A total of 45 aroma compounds were identified in dried Alkaya apricots (sulphured and unsulphured) by GC/MS, including esters (eight), norisoprenoids (six), terpenes (six), volatile acids (five), aldehydes (four), ketones (four), volatile phenols (four), lactones (three), pyrazines (three), furan (one), and hydrocarbon (one). Sulphuring treatment dramatically affected the distributions and concentrations of aroma compounds in dried apricots. In the unsulphured apricots, esters acids, lactones, norisoprenoids, and terpenes were in the highest abundance, while the terpene acids, hydrocarbon, lactones, and phenols were found in the greatest amount in the sulphured apricots. In general, the unsulphured apricots had higher levels of all compounds relative to the sulphured apricots with the exception of the terpenes. The levels of total compounds of the sulphured dried apricots were significantly different from the levels of the unsulphured apricots. Cabaroğlu et al. (2009) reported that concentrations of volatiles of dried apricots decreased with sulphuring and sulphuring doses. Göğüş et al. (2007) showed that the drying method of the apricot samples results in a change in compositions of their volatiles. Norisoprenoids, terpenes, lactones, esters, and pyrazines all have sensory impacts on apricot aroma.

Six terpene compounds were detected in the sulphured and unsulphured dried Alkaya apricots. The total concentration of terpenes determined in sulphured and unsulphured dried apricot samples were 0.804 μg/g and 0.584 μg/g, respectively. Among them, theaspirane-A and linalool were the most abundant. Terpenic alcohols such as linalool and α-terpineol with their low threshold values and fruity notes are responsible for the pleasant flavour of some apricot varieties (Guichard and Souty, 1988; Ozel and Gogus, 2010). Except linalool, there were significant differences between the level of terpenes in the sulphured and unsulphured samples ($P < 0.05$). Terpene levels in the sulphured samples were higher than that of unsulphured ones, likely because of the antioxidant effect of sulphur dioxide. It is well known that the sulphuring process prevents oxidation of some compounds and retards the degradation of others such as carotenoids (Bolin and Jackson, 1985; Mir et al., 2009). β-Cyclocitral was the only terpene found in higher levels in unsulphured samples, again likely due to degradation of carotenoids. It is reported that β-cyclocitral as well as β-ionone and dihydroactinidiolide are the main aroma degradation products of β-carotene in dried fruits (Mordi et al., 1993; Bechoff et al., 2010).

Norisoprenoids are volatile C_9–C_{13} fragments from the degradation of C_{40} carotenoids, which have extremely low aroma thresholds. They can be formed as a result of in vivo enzymatic degradation or postharvest thermal degradation of foods containing carotenoids. They have significant aroma impact in fruits (Mahattanatawee et al., 2005). The total concentration of norisoprenoids found in sulphured and unsulphured dried Alkaya apricot was 0.175 μg/g and 0.720 μg/g, respectively. Among norisoprenoids, β-ionone and α-ionone were the most abundant norisoprenoids compounds of Alkaya apricot. β-Ionone is often described as having a violet aroma and is an important contributor to the flavour of many fruits including apricot (Takeoka et al., 1990; Guillot et al., 2006). It has an extremely low odour detection threshold of 0.09 ng/mL (Ferreira et al., 2002). α-Ionone is described as having a floral and woody-like aroma and it has a low detection threshold of 2.6 ng/mL (Zalacain et al., 2007). In dried Alkaya apricots, these compounds are found in levels in excess of their detection thresholds and are therefore thought to be important contributors to dried apricot aroma. The formation of norisoprenoids, and especially β-ionone, from carotenoids by oxidation and heating was reported by Bechoff et al. (2010). The levels of norisoprenoids in the unsulphured dried Alkaya fruits were significantly higher than that of the sulphured ones ($P < 0.05$). This may indicate that carotenoid degradation was prevented or reduced by sulphuring treatment.

Lactones are known to possess fruity notes, which are reported as main aroma component of apricots (Guichard and Souty, 1988; Aubert et al., 2010; Ozel and Gogus, 2010). With regards to lactones, butyrolactone, dihydroactinidiolide, and dodecalactone were identified in both samples of Alkaya dried apricots. Dihydroactinidiolide, which possesses a weak black tea aroma, was the dominant lactone compound in both sulphured and unsulphured dried apricots at 0.271 μg/g and

Table 3. Concentration (µg/g dry matter) and retention indices of aroma compounds identified in sulphured and unsulphured Alkaya dried apricots.

Compounds	RI[a]	Id[b]	Sulphured	Unsulphured	P
Aldehydes					
Hexenal	1079	A	0.023	0.044	*
2-Ethyl-2-hexenal	1241	A	0.016	0.028	
(*E*, *E*)-2,4-Heptadienal	1426	B	-	0.053	
(*E*, *E*)-2,4-Decadienal	1780	B	-	0.043	
Total			0.039	0.167	*
Ketones					
4-Methyl-3-penten-2-one	1139	A	0.027	-	
4-Hydroxy-4-methyl-2-pentanone	1307	B	0.094	0.301	*
Acetophenone	1615	A	-	0.015	
3-Methylacetophenone	1725	B	-	0.014	
Total			0.121	0.329	*
Pyrazines					
2-Ethyl-6-methylpyrazine	1343	B	-	0.043	
2,3,6-Trimethyl-pyrazine	1365	B	-	0.066	
3-Ethyl-2,5-dimethylpyrazine	1432	B	-	0.062	
Total			-	0.171	
Furans					
Furfural	1410	A	0.040	0.090	*
Terpenes					
Theaspirane A	1503	B	0.248	0.157	*
Theaspirane B	1523	B	0.062	0.025	*
Linalool	1533	A	0.190	0.186	
β-Cyclocitral	1585	A	0.054	0.074	*
α-Terpineol	1674	A	0.122	0.085	*
Squalene	>2900	B	0.128	0.056	*
Total			0.804	0.584	*
Norisoprenoids					
A-Ionone	1806	A	0.036	0.044	*
B-Ionone	1910	A	0.026	0.230	*
2,3-Epoxy-β-ionone	1927	B	-	0.029	
Dihydro-β-ionone	1932	B	0.052	0.069	*
Dihydro-β-ionol	1959	B	0.022	0.070	*
3-Oxo-α-ionol	2639	B	0.039	0.279	*
Total			0.175	0.720	*
Lactones					
Butyrolactone	1562	A	0.048	0.337	*
Δ-Dodecalactone	2481	B	-	0.057	
Total			0.320	1.933	*
Hydrocarbons					
Naphthalene	1683	A	0.398	0.563	*

Table 3. (Continued).

Acids					
Hexanoic acid	1809	A	0.043	0.075	*
Dodecanoic acid	2455	A	-	0.244	
Tetradecanoic acid	2675	B	-	0.526	
n-Hexadecanoic acid	2891	B	0.546	1.459	*
Octadecanoic acid	>2900	B	-	0.056	
Total			0.589	2.360	*
Volatile phenols					
2-Phenylethanol	1868	B	-	0.038	
Benzophenone	2419	A	0.043	0.023	*
Vanillin	2491	B	0.075	-	
Propiovanillone	2639	B	0.201	0.294	*
Total			0.319	0.355	*
Esters					
Methyl hexadecanoate	2225	A	0.146	0.412	*
Ethyl hexadecanoate	2266	A	0.004	0.972	*
Ethyl octadecanoate	2476	A	-	0.053	
Methyl linoleate	2533	A	-	0.928	
Methyl vanillate	2539	A	0.104	-	
Ethyl linoleate	2555	B	-	0.510	
Methyl linolenate	2595	B	-	0.632	
Ethyl linoleolate	>2900	B	0.020	0.077	*
Total			0.273	3.583	*

[a]RI: Retention index on DB-Wax column.
[b]Id: Identification; A: identified by linear retention index and mass spectrum of reference compounds; B: identified by linear retention index and mass spectrum similar to published data or mass libraries.
Results are the means of three repetitions.
*Mean values are statistically different ($P < 0.05$).

1.539 µg/g, respectively. The unsulphured dried apricots contained significantly higher amounts of lactones than the sulphured ones ($P < 0.05$). Dihydroactinidiolide was also identified in the fresh Rouge du Roussillon (Guichard and Souty, 1988) and dried Hacıhaliloğlu and Kabaaşı apricot varieties (Cabaroğlu et al., 2009). It was reported that dihydroactinidiolide is produced from the heating or oxidation of beta-carotene (Nonier et al., 2004).

Furans and pyrazines are known to be the result of browning reactions. Pyrazines are an important class of compound in the flavour of food and are generally described as having roasted and nutty notes. They can dramatically impact the sensory aspects of food (Maga and Katz, 1982). Pyrazines were only identified in unsulphured dried Alkaya apricots at a level of 0.171 µg/g and were not detected in the sulphured dried apricots. Until recently, pyrazines were not reported in fresh apricots. Pyrazines both occur naturally and arise after heat processing of food by the Maillard reaction. The Maillard reaction is also known as nonenzymatic browning (Maga, 1992). Our findings showed that the sulphuring treatment before drying of apricot prevented the formation of pyrazines by Maillard reaction. The only furan compound found was furfural, identified in the sulphured and unsulphured dried apricots. The level of furfural in the unsulphured apricots (0.090 µg/g) was significantly higher than that of the sulphured ones (0.040 µg/g) ($P < 0.05$). This compound has a sweet and almond-like odour and is known to result from browning (Maillard) reactions (Ozel and Gogus, 2010).

The numbers and quantities of identified esters were very high in the unsulphured dried apricots and there were significant differences between concentrations ($P < 0.05$). Ethyl hexadecanoate and methyl linoleate were dominant among the esters of the unsulphured ones. All of them

were methyl and ethyl esters of long-chain fatty acids. These esters can be formed from oxidation of long-chain fatty acids in apricots. The amounts of esters found in sulphured dried apricots were much lower in comparison to the unsulphured dried apricots. This could be attributed to the antioxidant activity of sulphur dioxide. Most of the esters identified were also reported in Italian apricots by Nitz and Kollmannsberger (1993).

3.5. Conclusions

Sulphuring treatment affected the physicochemical characteristics and aromatic compositions of dried Alkaya apricots. Colour parameters highlight the darkening of the colour of the unsulphured apricots due to the severity of the browning process. Forty-five aroma compounds were found in sulphured and unsulphured dried Alkaya apricots. In general, the highest concentration of aroma compounds was found in unsulphured dried apricots, except for terpenes. Results showed that sulphuring treatment prevented or delayed the formation of new aroma compounds through the autoxidation of unsaturated fatty acids and thermal decomposition and/or Maillard reaction from nonvolatile precursors and preserved the terpene compounds with antioxidant activity. On the other hand, the natural drying process without sulphur treatment resulted in an increase in aroma concentration and formation of new aroma compounds such as norisoprenoids, lactones, pyrazines, and furfural by autoxidation and Maillard reaction during sun-drying. The main aroma compounds of the unsulphured dried apricots were β-ionone, α-ionone, linalool, β-cyclocitral, dihydroactinidiolide, ethyl hexadecanoate, pyrazines, and furfural according their concentrations and odour threshold values.

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