Determination of Aroma Volatile Composition of Ozone Treated Arils From Longterm-Stored Whole Pomegranate Fruits Using HS-SPME GC/MS Technique

Uzun Süre Depolanmış Nar Meyvelerinde Ozon Uygulamasının Nar Taneleri Uçucu Aroma Bileşiklerine Etkisinin HS-SPME GC/MS Tekniği ile Belirlenmesi

Research Article

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ABSTRACT

Long-term stored whole 'Hicaznar' pomegranate fruit arils were exposured to three different concentrations (0 mg/h/m^3, 5.2 mg/h/m^3, 10.4 mg/h/m^3) of ozon treatment and then minimally processed pomegranate arils stored at +5°C and 85-90% RH during 12 days. Effects of ozone treatment to 'Hicaznar' pomegranate arils aroma volatile compositions was were analyzed by using HS-SPME/GC/MS (Headspace Solid Phase Micro Extraction Gas Chromatography Mass Spectrometry) techniques. The results of research showed that aldehydes, terpenes, alcohols, acids and ester were main aroma volatiles in 'Hicaznar' pomegranate fruits arils at the end of storage. And terpens which are D- limonene, α-pinene, trans-a-bergamotene, 1.3.6.10-dodecatriene and caryophyllene percentage were higher in control than ozone treated fruits. However, the volatiles such as acetaldehyde, acetic acid and ethyl acetate were lower percentage in ozone treated fruits compared control one at the end storage.

Key Words
Pomegranate, volatiles, HS-SPME GC/MS, headspace.

ÖZET

Bütün olarak uzun süreli depolanan 'Hicaznar' nar meyvelerinden alınan tanelere, 0 mg/saat/m^3 5.2 mg /saat/m^3, 10.4 mg/h/m^3 olacak şekilde ozon uygulamasına maruz bırakıldıktan sonra 12 gün boyunca +5°C sıcaklık ve %85-90 oransal nem koşullarında muhafaza edilmiştir. Ozon uygulamasının nar meyvesi uçucu aroma bileşimine olan etkileri HS-SPME/GC/MS (Headspace Solid Phase Micro Extraction Gas Chromatography Mass Spectrometry) teknikleri kullanılarak belirlenmiştir. Çalışmada kullanılan 'Hicaznar' nar meyve suyu örneklerinde sırası ile aldehitler, terpenler, alkoller, asitler ve esterlerin temel uçucu aroma bileşikleri olduğu tespit edilmiştir. Terpen grubundan olan D- limonen, α-pinen, trans-a- bergamoten, 1.3.6.10-dodekatrien ve karyophilen bileşiklerinin kontrol grubu meyvelerinde ozon uygulanan meyvelerden daha yüksek olduğu tespit edilmiştir. Fakat Ozon ile muamele edilmiş meyve suyu bileşiminde asetaldehit, asetik asit ve etil asetat gibi uçucu aroma bileşiklerinin miktarının kontrol grubu meyvelerinde ozon uygulanan meyvelerden daha fazla olduğu belirlenmiştir.

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INTRODUCTION

Minimally processed fruits are not available in most of fruits throughout the year. However the fresh-cut of pomegranate fruit arils more popular due to the more suitable for service and easy to eat. The main problem is extent to shelf life of minimally processed pomegranate fruits arils used many tecnniques such as low and super atmospheric oxygen [1], Modified Atmosphere Packaging (MAP) and UV treatment [2], edible coating [3] and washing with sanitizing agents and low temperature storage and use of sanitizers chemicals as antimicrobial [4]. Fruits and vegetables are very perishable after harvest. To prevent to fruits and vegetables from microbial decay [4]. Chlorine and some similar compounds are widely used by the food industry. Lately due to the use of an sanitizers have forbidden in most of the European countries some of these reason which are mainly both human health, environment and fungucides resistant of patogen consumer and producer need to alternatives natural treatment for [5]. Lately ozone (O_3) treatment one of the promising application for food processing sector is alternative to conventional disinfectant for sterilization of fresh fruit and vegetables sectors during storage [5-7] Ozon is accepted as GRAS (generally recognize as safe) substance [8]. Pomegranate fruits demand increased by consumers due to the relationhip between antioxidant activity and health benefits and sensory perception of fruit [3,9]. However pomegranate fruit juice have low consistence of volatile and also lose of natural form volatile compounds compared to fresh fruit and also during processing and storage. The fresh fruits flavour depent on volatile compounds profile. The composition and quantity of -esters, aldehydes, ketones, alcohols, terpenes, furanones and sulphur effects aroma character of fruits [10]-. According to the literature knowledge, effects of ozone treatment on volatile of pomegranat fruit arils is very limited.

The aim of the present study was to determined effects of ozone treatment on volatile compounds of 'Hicaznar' pomegranate fruit arils after 12 days at +5 °C cold storage.

MATERIALS AND METHODS

Materials

Long term stored whole 'Hicaznar' pomegranate (*Punica granatum*) fruits arils were treated with three different ozone concentration at +7°C 85-90% for 1 h. Ozone treated pomegranate fruits arils were stored at +5°C, 85-90% relative humidity (RH) in polipropilen box (PPB) for 12 days. To evaluated effects of ozone treatment on minimally processed 'Hicaznar' whole pomegranate (*Punica granatum*) fruits were taken from the commercial company in Adana which is located in the Eastern Mediterranean part of Turkey. The longterm whole pomegranate fruits skin were removed for ozone treatment. Arils from whole fruit was carried out manually: (1) cut the fruit in half, (2) remove the edible arils and (3) put them into sterile sieved trays. Then arils were (4) exposured ozone air at 7°C, 85-90% with air circulation and (5) transferred in polypropylene box and then stored at 5°C prior to coating application. This study was conducted on cold stored long therm 'Hicaznar' pomegranate (*Punica granatum* L.) fruits. Minimally process pomegranate arils were treated for 60 min, according to previous researches in vegetables and fruit [11]. Control (C) was without any treatment (I): Arils were treated with ozon concentration 5.2 mg/h/m^3, (II): Arils were treated with ozon concentration 10.4 mg/h/m^3 and (III): After ozone treatment, 'Hicaznar' pomegranate were packed in PPT weighted 250 g then stored in +5°C 85-90% RH for 12 days. All treatments were replicated three times as an experimental unit for measurements and the results are given as mean ± standard deviation (SD). Automatic Headspace SPME technique was used for aroma extraction. The fruits were homogenized using fruit blender and weighed 5 g from the homogenate. This homogenate immediately transferred into the autosampler headspace vials (20 mL) adding 1 mL of NaCl (2%) and samples were held in place at 35°C for 20 min. Thermal desorption was performed in the injector glass liner at 250°C for 2 min. A library search was carried out using the Wiley, Nist, Flavor Libraries.

GC-MS Analysis

Volatile compounds of pomegranates were analyzed on an HP-GCD apparatus equipped with an HP-5 MS (60 m x 0.25 mm x 0.25 μm) fused-silica capillary column. The GC-MS system used for analysis was Agilent Technologies 6890N with Agilent 5975 27 inert XL Mass selective Detector (Agilent Technologies Co., Ltd., Palo Alto, USA) operating at 70 eV in EI (electron ionization) mode. Substances were separated on a fused silica capillary column, HP-5MS flexible 1 glass capillary gas chromatography column (30 m×0.25 mm×0.25 μm, Agilent Technologies Co., Ltd., Palo Alto, USA). The GC oven temperature was kept at 60°C for 10 min and programmed to 220°C at a rate of 4°C/min, and then kept constant at 220°C for 10 min, then programmed to 260°C at a rate of 1°C/min with splitless. The injector temperature was 250°C. MS were taken 6 at 70 eV. The mass range was *m/z* 35–425. A library search was carried out using the Wiley, Nist, Flavor GC–MS Libraries.

RESULTS AND DISCUSSION

Compared ozone treatment pomegranate arils volatile compounds to control treatment by using (HS-SPME/GC/MS) techniques at 12 day of storage showed Table 1. According to the results, the most abundant class of compounds were aldehyde, alcohol, terpenes, acids and ester in pomegranate arils respectively. Totaly there were six aldehydes, four alcohols, five terpenes, four acids, one esters and nine other compounds in pomegranate arils. There were five different terpenes which were alpha-pinene, D-limonene, trans-a- bergamotene, 1,3,6,10-dodecatetraene, caryophyllene detected in pomegranates arils. Limonene, alpha-pinene, trans-a- bergamotene and caryophyllene percentage level were higher in control fruits compared ozone treated fruits (Table 1). On the other hand there were the stress volatiles among the detected compounds such as hexanal. Hexanal was detected in all treatment however it was higher value in control fruit with 0.414%, 0.117% in 5.2 mg/h/m^3 and in 10.4 mg/h/m^3. Ozone treatment suppressed pomegranate arils percentage of hexanal compared to control at end of 12 days storage. One of the previous study [11] showed that hexanal production were stimulated by ozone treatment in carrot. In contrast with report [5], the ozone treatment of strawberry delayed senescence. Moreover [12] reported that ethanol, methanol and n-propanol prevent to fruit ripening. There is a correlation between plant tissue injurious and conversion of ethanol to acetaldehyde which repair plant injury [13]. In addition that, acetaldehyde percentage was higher in control fruits with 2.27% compared to ozone treated fruit as 0.625% in 5.2 mg/h/m3 and 0.427% in 10.4 mg/h/m3 so ozone treatment kept fruit acetaldehyde percentage lower. In addition to [14] showed that, both mechanical and water stresses significantly affected increased acetaldehyde in plant tissue and acetaldehyde production effect quality of fruits. Acetaldehyde may cause to ethanol and then metabolize ethyl acetate which are off- flavors [15]. And especially stress volatiles such as acetaldehyde and acetic acid were higher amount in control compared ozone treatment groups (Table 1). Both L(+) lactic acid and ethyl acetate were higher in control fruit also in 10.4 mg/h/m3 ozone dose compared to 5.2 mg/h/m^3 ozone treated group. Both exosure of higher ozone treatment as 10.4 mg/h/m^3 and control treatment may deleterious effects of pomegranate arils it may result of some off-flavors volatiles. According to the volatile compounds of minimally processed pomegranate fruit results, ozone treatment has promising effects on suppressed stress volatiles which caused off-odors volatiles.

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Table 1. Volatile profiles of 'Hicaznar' pomegranate fruits arils juice by HS-SPME GC/MS technique.

		Treatments		
Compounds	**RT**	**Control (%)**	**5.2 mg/h/m³ (%)**	**10.4 mg/h/m³ (%)**
Alcohols				
2-Nonen-1-ol	13.333	0.277±0.08	n.d	n.d
Phenol	18.252	0.476±0.3	0.294±0.1	0.234±0.6
4-methyl-1, 3-cyclohexen-1-ol,	13.817	0.255±0.04	0.183±0.2	n.d
1-Hexanol	10.503	n.d	0.117±0.1	0.740±0.2
Aldehydes				
Acetaldehyde	1.295	2.268±0.5	0.625±0.8	0.427±0.5
Octane	1.563	3.659±0.7	2.279±0.4	2.021±0.2
Hexanal	5.805	0.414±0.09	0.117±0.8	0.167±0.3
Octanal	9.429	0.065±0.02	0.246±0.03	0.103±0.01
Decanal	12.452	1.291±0.08	0.167±0.07	0.114±0.02
Nonanal	10.976	0.623±0.02	0.155±0.1	0.107±0.05
Acids				
L(+) Lactic acid	2.217	8.081±0.8	2.492±0.9	4.106±1.2
Acetic acid	11.985	1.392±0.3	0.779±0.09	0.685±0.1
Hexanoic acid	16.537	0.276±0.03	0.120±0.02	0.092±0.02
Sinapic acid	1.972	0.229±0.04	0.173±0.02	0.209±0.03
Ester				
Ethyl acetate	2.240	13.432±0.1	2.213±0.8	4.106±0.6
Terpenes				
α-Pinene	6.021	0.379±0.05	0.118±0.02	0.167±0.01
D-Limonene	7.568	0.865±0.06	0.533±0.1	n.d
Trans-a- bergamotene	13.420	1.380±0.2	0.952±0.07	0.159±0.01
1,3,6,10-dodecatetraene	14.278	0.240±0.01	0.145±0.01	0.109±0.04
Caryophyllene	13.596	0.357±0.02	0.176±0.04	0.090±0.01
Other compounds				
1,3-Dimethyl Benzen	8.898	n.d	20.530±0.6	0.192±0.06
Ethylbenzen	6.511	0.284±0.02	0.233±0.05	0.354±0.01
Benzen-1-methyl-4-(1-methylethyl)-	8.921	0.453±0.08	n.d	n.d
Benzen-1-methyl	7.276	n.d	n.d	0.108±0.01
Benzen, 1,3-dimethyl	7.538	n.d	20.530±0.5	n.d
3-Cyclohexen-1-ol,4-methyl-1-(1-methylethyl)	13.817	0.255±0.02	0.183±0.02	0.187±0.05
1-Cyclohexen-1-methanol,4-(1-methylethyl)	15.002	n.d	0.114±0.0	n.d
Benzene,1-(1,5-dimethyl-4-hexenyl)-4-methyl	15.825	0.119±0.05	0.119±0.03	0.068±0.03
Bicyclo [3,1,1] heptane, 6,6-dimethly-2-methlyne	6.010	0.379±0.01	0.118±0.01	0.286±0.06

*n.d: not detected

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