ISSN: 3062-3235

I-CRAFT AGRICULTURAL and FOOD TECHNOLOGIES

Determination of Aroma Compounds in Frozen and Fresh of Arnavutköy Strawberry Samples Using Two Different Spme Methods

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Abstract. The strawberry (*Fragaria × ananassa*) is classified among berry fruits, and its cultivation as a horticultural crop has a long historical background. Historical records indicate that a strawberry variety introduced from Istanbul to Ereğli many years ago was initially referred to as Arnavutköy and later became known as the Ottoman strawberry. Subsequently, this variety was hybridized with local landraces, particularly those referred to as Karaçilek, resulting in the development of new cultivars. The Arnavutköy strawberry is characterized by relatively small fruit size yet possesses a notably rich aromatic profile. Aroma is recognized as one of the most critical quality attributes of strawberries, with volatile compounds (VOCs) playing a pivotal role in determining consumer perception, acceptance, and overall preference. The identification of key volatile metabolites that confer the distinctive sensory attributes of the fruit is of considerable importance, as these compounds contribute to its fundamental sensory identity and uniqueness. In the present study, volatile composition analyses of fresh and frozen fruits of the Arnavutköy strawberry cultivar were conducted using gas chromatography–mass spectrometry (GC–MS) with using two distinct SPME fibers

Keywords: Arnavutköy, Strawberry, Aroma, Volatile compounds

1 Introduction

The strawberry, with its unique aroma, is one of the most popular fruits worldwide. Aroma is one of the most important determinants of strawberry (*Fragaria × ananassa* Duch.) flavour, directly influencing consumer preference and commercial quality. The characteristic aroma of strawberries arises from a highly complex mixture of volatile organic compounds (VOCs), which include esters, furanones, terpenoids, aldehydes, alcohols, and sulfur-containing compounds (Schwieterman et al., 2014; Ulrich et al., 2024). To date, more than 350 VOCs have been identified in strawberries, although only a limited number exhibit significant odour activity due to their low perception thresholds (Pérez et al., 2021). Among them, esters such as ethyl butanoate, ethyl hexanoate, and methyl butanoate contribute fruity and sweet notes and are recognized as the predominant aroma-active group in ripe fruits (Wang & Seymour, 2017). Furanones, particularly 2,5-dimethyl-4-hydroxy-3(2H)-furanone (furaneol) and 2,5-dimethyl-4-methoxy-3(2H)-furanone (mesifuran), provide sweet, caramel-like nuances and increase

https://doi.org/10.65888/icraft.3.1.6

markedly during ripening (Ulrich et al., 2024). Terpenoids such as linalool and nerolidol impart floral and citrus-like notes, whereas aldehydes and alcohols, including hexanal, trans-2-hexenal, and 1-hexanol, are responsible for fresh, green aromas (Pérez et al., 2021). Despite their low concentrations, sulfur volatiles such as methanethiol can exert a strong sensory effect due to their very low odour thresholds (Sánchez-Sevilla et al., 2017). The biosynthesis and relative abundance of these VOCs are strongly influenced by genotype, fruit maturity, and postharvest conditions, all of which determine the overall flavour quality perceived by consumers (Ulrich et al., 2024). In the present study, volatile composition analyses of fresh and frozen fruits of the Arnavutköy strawberry cultivar were conducted using gas chromatography–mass spectrometry (GC–MS) with using two distinct SPME fibers.

2 Material and Method

2.1 Material

In this study, frozen and fresh samples of the Arnavutköy strawberry variety were used. The Arnavutköy variety is an aromatic, aromatic, and biotic stress-resistant local variety. It is preferred in breeding programs in Turkey due to its tolerance to Phytophthora infestans (Kepenek 2016).

2.2 Method

2.3 The determination of Volatile Compounds

Volatile compounds were extracted using solid phase microextraction (SPME). For each sample, 1 g of homogenized strawberry was placed in a headspace vial with 1 mL of $CaCl_2$ and incubated for 30 minutes at 40 °C. A 85 µm CAR/PDMS (carboxen/polydimethylsiloxane; light blue) SPME fiber (Supelco Co., Bellefonte, PA, USA) was used for extraction. The adsorbed volatile compounds were analyzed using a Shimadzu GC-2010 Plus GC-MS system (Shimadzu Corporation, Kyoto, Japan) equipped with an HP-Innowax column (30 m × 0.25 mm i.d., 0.25 µm film thickness) and helium as the carrier gas. The GC oven temperature was initially held at 40 °C, then increased to 260 °C at a rate of 5 °C/min, and maintained at 260 °C for 40 minutes. Compound identification was based on library searches using Wiley, NIST, and Flavour databases. Relative percentages were calculated from the total ion chromatograms using Shimadzu's GC-MS Postrun Analysis software (GC-MS-QP2010, Japan). Tentative compound identification was performed by comparing mass spectra with those in the NIST08 library (Kafkas et al., 2018b).

3 Results and Discussion

Aroma is a very important parameter in strawberry quality. Therefore, there are many studies related to aroma. In a study conducted within the borders of Aydın, aroma analyses were performed using GC-MS on Florida Fortuna, Rubygem, and Sabrina strawberry varieties. Upon examining the results, it was reported that, according to the aroma composition analysis results obtained using GC-MS, 16, 18, and 20 volatile compounds were identified in the Florida Fortuna, Sabrina, and Rubygem varieties, respectively, and that esters, which generally give fruit scent, were observed to be the active compounds in all strawberries (Görgüç, et al., 2019). Volatile compounds in strawberries are responsible for their aroma and contribute to the flavor of fresh strawberries. These compounds constitute only 0.01-0.001% of the fruit's fresh weight. However, they have a significant effect on strawberry quality (Buttery, 1981). Fresh strawberries produce numerous volatile compounds; among these, esters are the most abundant in terms of both quantity and quality. Research indicates that there are 131 different esters in strawberry aroma (Latrasse, 1991). In addition to esters, aldehydes (Schreier, 1980) and furanones (Larsen and Poll, 1992) account for 50% of strawberry volatiles among other compound classes. Only a small fraction of the hundreds of volatile compounds produced by fresh strawberries contribute to the fruit's aroma and taste. The characteristic aroma is a mixture of a number of volatile compounds; no single "character effect" compound is responsible for the strawberry aroma. A compound's contribution to the aroma depends on its odor threshold and concentration in the fruit (Forney, et al., 2000; Kafkas, et al., 2018a). In another study conducted, the enantiomeric ratios of 8 volatile compounds (methyl 2-methylbutanoate, ethyl 2-methylbutanoate, 2-methylbutanoic acid, linalool, α-ionone, γ-decalactone, γ-undecalactone, δ-dodecalactone) in 7 strawberry aromas and 14 strawberry syrups from 6 strawberry varieties. The volatile compounds identified at the end of the study, γ-Decalactone (enantiomeric ratios; 100/0, 100/0, 99/1, 99/1, 100/0, and 99/1 in strawberries; 100/0 in 3 natural aromas, 100/0 in natural flavored syrup) were found to be the most important indicator of synthetic and natural strawberry flavor. This was followed by ethyl 2-methylbutanoate (enantiomeric ratios: 0/100, 5/95, 5/95 in 3 natural aromas, 0/100 in natural flavored syrup), and the study indicated that the best resolution was in α-ionone (RS>4). Furthermore, in the investigation of the enantiomeric ratios of 7 chiral (compound molecules containing two hydroxyl groups) volatile compounds and uniquely selected strawberry samples, the use of the CP-Chirasil-Dex CB chiral column was found to offer more reliable possibilities for the determination of natural strawberry aroma in complex matrices (Průchová et al., 2022). In our study, aroma components were detected in fresh and frozen Arnavutköy strawberries using two different SPME cartridges, red and gray. The results obtained from the analysis of frozen samples using the red SPME are presented in Table 1 and Figure 1.

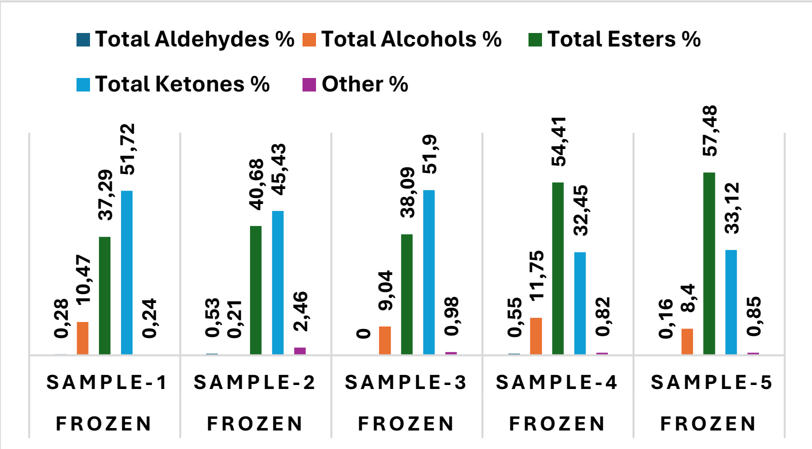

Fig. 1. Determination of Volatile Compounds of Frozen Arnavutköy Strawberries with using red SPME (%)

According to this analysis, aroma components were found in the following ranges: total aldehydes (0.16-0.55%), total alcohols (0.21-11.75%), total esters (37.29 - 57.48%), total ketones (32.45-51.90%), and other components (0.24-0.98%). The results obtained from the analysis of fresh Arnavutköy samples using gray SPME are presented in Table 2 and Figure 2.

Table 1. Determination of Volatile Compounds of Frozen Arnavutköy Strawberries with using red

Compound name	Frozen Sample-1	Frozen Sample-2	Frozen Sample-3	Frozen Sample-4	Frozen Sample-5
Aldehydes(-al)					
Nonanal	0.1	0.34	-	0.19	-
Undecanal	0.18	0.19	-	0.22	0.16
Farnesal	-	-	-	0.14	-
Total	0.28	0.53	-	0.55	0.16
Alcohols(-ol)					
Nonan-2-ol	0.13	-	0.12	0.13	-
2-Tridecanol	46213,00	25112,00	22494,00	22920,00	46211,00
Phenol, 2-methoxy-4-(2-propenyl)	0.14	-	-	0.34	0.18
1-Dodecanol	0.13	-	-	-	-
1-Decanol	-	-	-	0.22	0.15

beta.-Citronellol	-	0.21	0.31	0.44	-
Total	17441,00	32782,00	46121,00	27699,00	46120,00
Esters(-ate)					
Octanoate <ethyl->	0.35	0.18	0.23	0.13	0.13
Propanoic acid, 2-methyl-, 2-methylpropyl ester	0.91	-	-	-	-
Octanoic acid, methyl ester	0.13	-	-	-	-
acetic acid, hexyl ester	0.47	0.18	0.18	-	-
Acetic acid, phenylmethyl ester	-	-	0.11	-	-
acetic acid, 2-ethylhexyl ester	46268,00	46328,00	17564,00	46266,00	46235,00
decanoic acid, methyl ester	0.26	0.35	0.3	0.39	0.43
decanoic acid, ethyl ester	0.25	0.25	0.31	0.47	0.56
Acetic acid, dodecyl ester	-	-	0.2	0.36	0.39
acetic acid, decyl ester	46388,00	46082,00	13516,00	27030,00	34335,00
Acetic acid, nonyl ester	-	-	0.09	-	-
dodecanoic acid, methyl ester	0.62	41306,00	42005,00	26299,00	27760,00
dodecanoic acid, ethyl ester	0.47	0.95	0.8	46266,00	14977,00
butanoic acid, 2-octyl ester	0.32	0.42	0.27	12785,00	21186,00
capronate <ethyl->	0.32	-	-	-	-
Propanoic acid, 2-octyl ester	-	-	-	-	0.11
2-octanol, acetate	0.43	0.41	0.49	0.34	0.37
butyl decanoate	0.13	0.45	-	-	-
myrtenyl acetate	0.1	0.14	0.24	-	-
methylanthranilate	46024,00	16803,00	0.95	0.6	0.41
cinnamyl acetate	0.56	0.85	0.74	15342,00	46113,00
Tridecyl acetate	0.13	-	-	-	-
Undecyl acetate	-	-	0.12	-	-
2-Heptadecanol, acetate	24.82	27.64	26.57	41.52	42.52
trans-2-Dodecen-1-ol, acetate	0.39	0.78	-	-	-
(z)-3-phenyl-2-propenoic acid, methyl ester	-	0.16	0.13	0.15	0.09
trans-2-Dodecen-1-ol, acetate	-	-	0.6	-	-
5-Tetradecen-1-ol, acetate, (Z)-	-	0.15	0.12	46327,00	43101,00
n-Capric acid n-heptyl ester	-	-	0.31	0.35	0.47
iso butyl decanoate	-	-	-	-	0.14
Cyclooctanol, acetate	-	-	-	-	41640,00
Caprylate <hexyl->	0.17	0.26	0.19	-	-
lauric acid, n-octyl ester	-	0.23	0.14	-	-
Hexanoic acid, 3-tridecyl ester	-	-	-	0.34	0.44

Hexanoic acid, octyl ester	-	-	-	0.24	0.29
Total	37.29	40.68	38.09	54.41	57.48
Ketons(one)					
2-Undecanone	40.72	31.22	41.02	21.46	21.47
2-Heptanone	0.27	-	-	-	-
2-Nonanone	0.93	0.42	0.6	0.28	0.22
2-Pentadecanone	0.71	35065,00	0.99	18994,00	34700,00
Ketone, 1-cyclohexen-1-yl phenyl	-	-	-	0.34	0.31
.gamma.-decalactone	-	-	-	0.23	-
Farnesene <(E,E)-, alpha.->	0.12	-	-	-	-
2(3H)-Furanone, 5-hexyldihydro-	0.35	-	-	-	-
2-Tridecanone	22859,00	30621,00	47362,00	22859,00	42979,00
Total	51.72	45.43	51.9	32.45	33.12
Other					
Dodecanoic acid	0.12	-	-	-	-
Pentadecanoic acid	-	-	0.11	0.14	-
Tetradecane	0.12	-	-	-	-
4-octylbutan-4-olide	-	0.2	0.11	-	-
4-hexylbutan-4-olide	-	0.59	0.39	-	0.13
Dodecanoic acid	-	0.13	-	-	-
pentan-1,3-diol,diisobutyrate, 2,2,4-trimethyl-	-	0.15	0.09	-	-
benzene, methyl-	-	43101,00	-	-	-
.beta. elemene	-	0.21	0.18	-	0.11
2-Hexadecen-1-ol, 3,7,11,15-tetramethyl	-	-	-	0.32	0.41
Cytidine	-	-	-	0.22	-
Palmitic acid	-	-	-	0.14	0.2
2-Methoxy-6-vinylnaphthalene	-	-	-	-	-
Total	0.24	16834,00	0.98	0.82	0.85

Table 2. Volatile Compounds of Fresh Arnavutköy Strawberries with using gray SPME (%)

Compound name	Fresh Sample-1	Fresh Sample-2	Fresh Sample-3	Fresh Sample-4	Fresh Sample-5
Aldehydes(-al)					
Undec-8-enal <cis->	22678,00	46083,00	-	42370,00	-

Hexanal	-	0.95	-	-	-
Furfural	-	-	-	-	12785,00
Nonanal	14277,00	44287,00	0.68	46143,00	-
Dec-2(E)-enal	-	-	-	46054,00	-
Deca-2(E),4(E)-dienal	-	-	0.8	-	-
Propanal, 2-oxo-	-	-	-	-	0.39
Octanal	-	46328,00	-	-	-
2-Decenal, (E)-	-	15373,00	0.77	-	-
Hydroxy methyl furfural	-	30682,00	-	-	-
2-Dodecenal	-	-	46023,00	-	-
5-methyl furfural	-	-	-	-	0.54
furan-2,5-dicarboxaldehyde	-	-	-	-	0.63
2-Furancarboxaldehyde, 5-(hydroxymethyl)-	14.99	-	18.62	46177,00	50.4
Total Aldehydes	20,00	13.83	21.88	17349,00	53.31
Alcohols(-ol)					
2-Tridecanol	16132,00	46360,00	18688,00	34366,00	0.77
Phenol, 4,4'-(1-methylethylidene)bis-	-	31594,00	15008,00	24929,00	0.45
Syringol <4-methyl->	-	-	-	-	0.39
2-Furanmethanol	-	-	-	-	0.52
Phenol, 2-methoxy-4-(2-propenyl)	44409,00	-	-	-	-
Silanediol, dimethyl-	18080,00	31260,00	-	46117,00	-
Total Alcohols	19.14	20.83	33725,00	24442,00	41306,00
Esters(-ate)					
methylanthranilate	46205,00	46237,00	-	-	-
Silanediol, dimethyl-ester	-	-	29037,00	-	-
(E)-Ethyl Undec-2-enoate	-	-	-	-	0.89
Cinnamyl acetate <(E)->	-	43101,00	33970,00	15342,00	-
5-Tetradecen-1-ol, acetate, (Z)-	-	-	0.72	46025,00	-
1,2,3-Propanetriol, monoacetate	-	-	-	-	46023,00
Caproate <methyl->	-	-	-	46023,00	-
Capryl acetate	-	-	-	-	46143,00

2-Heptadecanol, acetate	-	-	-	-	43132,00
Laurate <ethyl->	-	-	-	1,00	-
2-Propenoic acid, methyl ester	-	-	-	-	0.39
Butyric acid, 3-tetradecyl ester	-	-	0.47	-	-
trans-2-Dodecen-1-ol, acetate	-	-	46084,00	-	-
benzoic acid, 2-amino-, methyl ester	-	-	24198,00	24473,00	-
Dodecanoic acid, methyl ester	-	-	0.43	-	-
Undecyl acetate	-	-	0.55	-	-
methyl 2-furoate	-	-	-	-	45658,00
2-Heptadecanol, acetate	35582,00	46371,00	11628,00	13.62	-
2-Hexen-1-ol, acetate, (E)-	-	1,00	0.56	-	-
Acetic acid, decyl ester	-	43101,00	-	-	-
Acetic acid, 2-ethylhexyl ester	-	36161,00	0.53	31413,00	-
Acetic acid, hexyl ester	-	18629,00	0.62	-	-
Total Esters	24716,00	25.78	32.59	23.77	31564,00
Ketons(one)					
2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	23743,00	-	46813,00	-	13.27
2-acetyl-2-hydroxy-gamma-butyrolactone	-	-	-	-	0.66
2-Pentadecanone (CAS)	-	-	0.35	23012,00	-
2-Undecanone	15.51	23.56	13.48	24.72	36220,00
Tetradecalactone <delta->	-	-	-	46357,00	-
Nonadecanone	-	-	-	45292,00	-
2-Nonanone	-	-	0.44	-	-
Methyl undecyl ketone	-	22313,00	-	-	-
2-Tridecanone	2,00	-	46175,00	46026,00	0.75
Total Ketones	19.16	26.17	19.61	32.72	18.67
Other					
Pentadecanoic acid	12632,00	30773,00	15738,00	16862,00	27030,00

Stearyltrimethylammonium chloride	-	46175,00	-	-	-
Cetrimonium Bromide	-	-	0.54	-	-
2-Propenoic acid, 3-phenyl-	-	-	0.53	-	-
2-Propanone, 1-hydroxy-	-	-	-	-	0.53
Nonanoic acid	-	-	0.53	-	-
Acetic acid	-	-	-	-	46117,00
2-Hexadecen-1-ol, 3,7,11,15-tetramethyl-	-	-	30317,00	-	-
Guanosine	-	-	-	-	32174,00
Caprylic acid <4-methyl->	-	-	-	-	0.95
Formic acid	-	-	-	-	11689,00
9-Octadecenoic acid, (E)-	-	-	-	-	0.38
2-Propenamide, 2-methyl-N-phenyl-	-	18994,00	0.43	46174,00	-
D-Allose	-	-	-	-	0.46
2-Propenoic acid, 3-phenyl	-	-	-	-	0.65
Acetic acid	34029,00	-	27181,00	46055,00	-
4H-pyran-4-one, 3-hydroxy-2-methyl-	-	-	-	-	46174,00
d-Mannose	-	-	-	-	32143,00
Hexanoic acid	27760,00	-	-	-	-
N,N-Dimethyl Pentadecylamine	16.29	-	-	-	-
Dodecanamide, N,N-bis(2-hydroxyethyl)-	-	-	0.58	-	-
Benzene, methyl-	-	26359,00	-	43466,00	-
Dodecanoic acid	-	-	-	32509,00	-
Methane, tetraiodide	-	-	11841,00	-	-
Heptadecene (8-) carbonic acid (1)	-	45658,00	-	-	-
2-Propenoic acid, 3-phenyl-	46204,00	-	-	-	-
Total	32.02	13.39	46101,00	12693,00	17.43

Accordingly, total aldehydes (7.47-53.31%), total alcohols (2.13-20.83%), total esters (6.86-32.59%), total ketones (18.67-32.72%), and other compounds (10.34-32.02%).

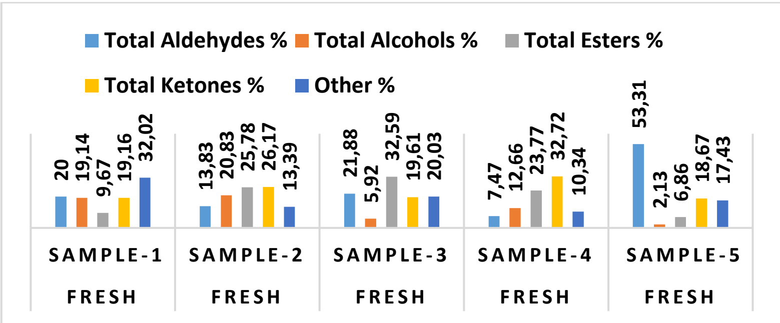

Fig. 2. Determination of Volatile Compounds of Fresh Arnavutköy Strawberries with using Gray SPME (%)

4 Conclusion

According to the results of this study, the highest total aldehyde content in fresh Arnavutköy fruits was detected in Sample-5 using gray SPME, at 53.31%. In addition, the highest total alcohol and total ester ratios in fresh Arnavutköy fruits were measured as 20.83% and 25.78% in Sample-2 using gray SPME. Furthermore, the highest total ketone ratio was found to be 20.03% in Sample-3. In the analysis performed with red SPME on samples of the frozen Arnavutköy strawberry variety, the highest ester ratio was detected in Sample-5 at 57.48%. While the highest ketone ratio was found in Sample-3 at 51.9%, the highest aldehyde was observed at 0.55% and alcohol ratios at 11.75% in Sample-4. This study will shed light on more comprehensive studies involving other Arnavutköy species.

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