Chapter

Volatile Components of Strawberries

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Abstract

Strawberries of such cultivars as "Ducat", "Honey" and "Polka" were studied to define the content of aromatic volatiles using the methods of highly efficient liquid chromatography. About 49 components were identified in the composition of volatiles of ripe strawberries, namely esters, aldehydes, ketones, furanone, organic acids, aroma compounds, lactones, terpenic compounds, and alkanes. Their shares are the following: esters—12.8–41.8%, aldehydes—5.9–15.9%, ketones—8.7–35.6%, furanone—22.7–24.4%, and organic acids—2.47–21.85%. Depending on a cultivar, typical volatile components of strawberries are ethyl butanoate (10.1–30.65%), trans-2-hexenal (5.31–15.55%), acetoin (8.20–35.67), 2.5–dimethyl-4-methoxy-3(2H)-furanone (mesifurane) (19.08–19.92%) and 2.5-dimethyl-4-hydroxy-3(2H)-furanone (3.43–4.40%). A peculiar feature of volatile compounds of Polka strawberries is the highest ester share—41.77% of total content of volatiles, for Ducat strawberries it would be the share of ketones (35.88%), and for Honey strawberries—γ-decalaktone (12.41%). A high aroma activity of ripe strawberries is recorded on 2.5-dimethyl-4-methoxy-3(2H)-furanone (mesifurane) and 2.5-dimethyl-4-hydroxy-3(2H)-furanone (furaneol). Sweet, caramel flavors are typical for strawberries of the studied cultivars. Strawberries of Polka cultivar have a pronounced aroma.

Keywords: strawberries, volatiles, compounds, activity of volatile components

1. Introduction

Strawberries are valued for their harmonious taste and attractive, pronounced aroma, which is formed under the effect of volatiles. Strawberry aroma is known to be very specific and more than 360 compounds constitute its components, such as esters, aldehydes, ketones, alcohols, lactones, terpenic compounds, furanone [1–4]. Esters are considered to be the major components (over 130 different esters were identified); according to various data, they constitute 25–90% of the total amount of volatiles of ripe strawberries and add some flower or fruit flavors to strawberries [1, 2]. About 49 components were identified in volatile compound composition in strawberry varieties "Polka", "Ducat" and "Honey": esters, aldehydes, ketones, furanone, organic acids, aroma compounds, lactones, terpenic compounds, and alkanes. The most meaningful ones are: esters—12.8–41.8%, aldehydes—5.9–15.9%, ketones—8.7–35.6%, furanone—22.7–24.4% and organic acids—2.47–21.85% [5].

Aldehydes and furanone represent a large amount of volatile compounds of strawberries, their share being 50%. The latter adds a grass, sweet, or caramel flavor to the strawberry aroma [6–8]. Instead, according to other data, furanone is the main source of the strawberry aroma. Their level in the most aromatic cultivars exceeds a corresponding indicator of other cultivars by 20 times [4]. A small amount of aroma volatiles can be referred to as terpenic and sulfur compounds which can also have a considerable impact on strawberry aroma [9]. The most important chemical compounds which form strawberry aroma methyl butanoat, ethylbutanoate, 2-methylbutanoat, ethyl hexanoat, methylhexanoat, methyl 2-methylpropanoat [10], 4-hydroxy-2,5-dimethyl-3(2H)-furanone and 4-methoxy-2,5-dimethyl-3(2H)-furanone [6, 11, 12], (Z)-3-hexenal; butan-2,3-dion and linalool [13].

The most common ethers are: ethyl butanoate, butylacetate, ethylcrotonate, ethylcapronate, ethyl 3-hydroxycapronate, which give them fresh grass tone. Among aldehydes, those will be trans-2-hexenal and pentanal. Palmitic acid, carvone, and acetoin were found in all studied strawberry cultivars. Terpenic compounds are represented by nerolidol and linalool which give spicy notes to a strawberry flavor [14, 15]. Tetradecane was defined in the alkane class. Furanone were represented by 2,4-dioxy-2,5-dimethyl-3(2H)-furan-3-one, 2,5-dimethyl-4-methoxy-3(2H)-furanone (mesifurane) and 2,5-dimethyl-4-hydroxy-3(2H)-furanone (furaneol) [5].

Genetic peculiar features of a cultivar, a maturity degree, and storage conditions have an effect on the composition and concentration of volatiles [9]. The aroma of strawberries can change during storage [3, 16] and processing them into canned products [17]. For instance, the availability of methyl ester is a characteristic feature for "Hokowase", "Kent", "SengaGigana" and "Annapolis" strawberries, the share of which is equal to 70% of the total content of volatiles, whereas the availability of ethyl3-methylbutonoat and 3-methylacetate is more typical for cultivars "Kent" and "Micmac", and that of hexylacetate—for "Honeoye". Linalool was found in "SengaSengana" and "Annelie" strawberries [1].

Ethylbutanoate (10.1–30.65%), trans-2-hexenal (5.31–15.55%), acetoin (8.20–35.67), 2,5-dimethyl-4-methoxy-3(2H)-furanone (mesifurane) (19.08–19.92%) and 2,5-dimethyl-4-hydroxy-3(2H)-furanone (3.43–4.40%) were typical compounds for the flavor of the strawberry varieties studied. In addition, strawberries of Honey variety showed high content of Hexanoic (caproic) acid (9.54%) and Hexadecanoic acid (5.08%) [5].

The aroma of strawberries is formed in the process of ripening under the effect of enzymes. It is a known fact that when the strawberry color changes from white to a total red one the content of volatiles in them increases by 14 times. In green, unripe strawberries aldehydes and alcohols predominate and they add grass, green aroma, and in ripe strawberries—esters and furanone [10]. According to [18], EA and aldehydes predominate in green strawberries, in white berries—ketones and alkanes, and in red strawberries—esters, acids, furanes, and alcohols [18]. I has been experimentally proved that in the process of ripening the concentration of grass aroma components, such as hexanal, trans-2-hexanol and cys-3-hexenylacetat, decreases gradually [19]. Instead, the total ether content, including esters, increases, the content of furanone and lactones grows rapidly, the former were not found in green strawberries. Besides, during ripening the concentration of general aldehydes, aromatic compounds and alcohols undergo change [4].

Aldehydes and esters result from the enzymatic oxidation of lipids and a fermentative bio-synthesis of alcohols and acids, the latter occurs with the participation of alcohol-dehydrahenaza [3]. Alcoholacetyltransferaza plays a decisive role in a taste bio-synthesis during strawberry ripening through the formation of esters which are the main components of strawberry volatiles [20], this takes place together with volatile free fatty acids in mesocarp cells and strawberry protoplasts [21]. The role of Fragaria 3 ananassaxinon-oxydoreductasa in bio-synthesis of 2,5-dimethyl-4-hydroxy-3(2H)-furanone has been proved [22], and the formation of 2,5-dimethyl-4-hydroxy-3 (2H)-furan-3-one catalyzes β-glucozidaza [23, 24].

The environmental conditions, in particular lighting, are the major factor in the formation of a strawberry aroma. It has been proved that shading by 47% leads to a considerable decrease in the concentration of hexanal, hexanal, ethyl-methyl butyrate, and methylbutyrat in strawberries, as compared with well-lighted plants [21], which is due to the deceleration of a photosynthesis process in the plants, and, as a result, the decrease of the number of primary metabolism products; the latter are the raw materials for the synthesis of volatiles [25, 26].

2. The change of strawberry volatiles during the storage in a refrigerated state

When strawberries are harvested, their aroma can enhance during the first days of the storage which results from the fruit aging and the increased synthesis as well as the accumulation of volatile esters in fruit tissues and/or a resistance decrease to the diffusion of these compounds from the fruits because of the tissue aging [23]. It has been proved that during four days of the storage at a temperature of 15°C the concentration of volatiles in the strawberries increases by 7 times; besides, according to the data of some authors the content of esters and furanone increases [9].

The refrigerator storage of strawberries can cause changes in their aroma: its losses or gains of some outside, this decreases quality considerably [3]. Any storage method for strawberries facilitates the losses of aromatic compounds [25]. Both temperature and storage duration have a serious effect on fruit aroma [27].

According to the data of Pelayo-Zaldívar et al. [28], the loss of aroma of strawberries during the storage can be due to the accumulation of acetaldehyde and ethanol in them, the additional synthesis of methyl ether, and the formation of a new profile of aromatic compounds. Besides, the losses can be caused by the changes of non-volatile components of aroma such as sugars and citric acid, the changes of phenol compounds, and the increase of their resistance under the effect of low temperatures. El Hadi et al. [27] consider the temperature to be the main factor that influences fruit taste and aroma.

Pérez with the co-authors [29] states that during the storage strawberry aroma changes and it occurs due to the slowdown of the formation of some volatile esters and the sharp reduction of furaneol amount. Ozcan and Barringer [30] present the data about a low activity of the enzyme of spirit, acetyltransferase in strawberries during the storage at 1°C.

According to Larsen and Watkins [31], the storage of strawberries at high content of carbon dioxide in the atmosphere enhances the resistance to physiological decay, but it slows down the development of aroma.

It was proved that as a result of the refrigerator storage of strawberries, cultivar Polka, at temperature 0 ± 1°C and air relative humidity 90–95% during 9 days the content of volatile compounds decreased by 36.3%, that of esters—by 66.0%, which was caused by lowering the temperature and weakening the activity of the enzyme alcoholdehydrohenasa in the conditions of the lowered temperature [32].

During the storage, the content of furanes also decreased—by 45.3%. Similar data was received when the sum of acids, ketones, and terpenes was determined, their share decreased by 9.7, 32.4, and 64.9%, respectively, as compared with the initial content [5]. A serious decrease was typical for some compounds, namely, ethyl butanoate—by 6.8 times, ethyl crotonate—by 11.3 times, ethyl caproate—by 6.1 times. The content of furanes decreased by 1.6 (mesifurane) and by 3 times (furaneol).

Along with a number of biochemical transformations in strawberries after the storage, their organoleptic properties also change. For instance, when strawberries are stored in a modified atmosphere not only the change in aroma, consistency, and a degree of sweetness are recorded; some undesirable features appear such as rancidity, fermented smell, etc. Also, strawberries that were stored in the atmosphere with a high content of carbon dioxide showed undesirable features more often [33].

2.1 Change of volatile compounds of frozen strawberries

The freezing process causes changes in the aromatic profile of strawberries. For instance, the storage of strawberries within one week with a follow-up defrosting at the ambient temperature facilitates the enhanced level of acetaldehyde, cis-3-hexenal, hexenal, ethylacetate, and methyl acetate [34]. The scientists [35] advise about the worsening of strawberry aroma during the freezing and continuous storage. It has been proved that ethers, which are characteristic components of fresh strawberry aroma, in fact, are not recorded in frozen berries, whereas the content of carbon compounds remains at the same level.

The appearance of an unpleasant aroma in frozen berries is associated with the formation of H_2S which releases due to pH decrease of cell sap resulted from the cell damage during the freezing process [36]. According to the data presented by Schreier [37], the freezing process leads to the reduction of the concentration of the majority of aromatic compounds, but the content of 2,5-dimethyl-4-methoxy-3(2H)-furanone in them increases. Douillard and Guichard [38] point out the increase of the concentration of nerolidol and the decrease of the ether share in frozen berries.

2.2 Aroma of canned strawberries

The processing of fruits and berries has a serious impact on the taste and aroma of the finished output, the reduction of its effect favors quality preservation. The aroma of the processed strawberry output depends, to a great extent, on fresh berries.

The aroma of strawberry compotes (stewed fruit) is formed under the effect of furanone (15.5–23.5%) and aromatic acids (48.4–76.1%) which add sweet caramel and sour-sweet scents [5].

The aroma of strawberry compotes (stewed fruit) consists of a mixture of compounds: esters, aldehydes, aromatic spirits, aromatic acids, lactones, ketones, furanone, and terpenes. Among them, a large share belongs to acids—48.4–76.1 from the total content of volatiles and to furanes—15.5–23.5%. A considerable amount of aromatic spirits—21.1% and esters—4.2% were recorded in compotes made of Polka strawberries.

Typical volatile compounds of the compotes made of strawberry cultivars Polka, Ducat, and Honey are hexanoic (caproic) acid (7.6–23.3% from the total content of volatiles), 2-ethylhexanoic (capronic) acid (6.9–8.6%), trans-cinnamic acid (22.5–30.2%) which add sour-sweet aroma to them.

Large amounts of 2,4-dioxy-2,5-dimethyl-3(2H)-furan-3-one (1.1–2.3%), 2,5-dimethyl-4-methoxy-3(2H)-furanone (mesifurane) (7.6–16.0%) and 2.5-dimethyl-4-oxy-3(2H)-furanone (6.4–9.8%) are recorded in compotes (stewed fruit); they all add sweet caramel scents [5].

The presence of furfural (0.3%) and 5-hydroxymethylfurfural (0.2%) in compotes confirms a non-fermentative darkening during heat treatment [39, 40].

In addition to the above-mentioned compounds, ethyl butanoate (3.2%), which adds fresh grassy scents, and hydrocinnamicalcohol (15.9%) make their serious contribution to the aroma of the compotes made of cultivar Polka. Vanillin was recorded in the compotes made of cultivars Ducat and Honey, adding typical vanilla scents; its concentrations were 1.4 and 0.8%, respectively. There was γ-decalactone (3.2%) in the composition of volatile compounds of the compotes made of cultivar Honey which added fruit, a sweet scent to aroma [15].

The compotes had 2H-pyran-2,6(3H)-dion (0.7–2.0%), 3,5-hydroxy-2-dimethyl-4H-pyran-4-on (0.2%) and 3.4-dihydropyran (0.2–0.4%), which were the products of Mayar's reaction, resulted from the reaction of glucose with glutamine acid, glycine, butalamine, lisyn,hydroxyproline and/or fenilalanine [39].

In strawberry compotes terpene compounds include linalool (0.5–0.6% depending on a cultivar), α-Terpineol (0.2–0.7%), which were present in fresh strawberries [16], they add spicy scents to berry aroma, and also oxydebisabolol A (0.1–0.8%), trans-linalool oxide (0.3–0.5%), which were not found in fresh strawberries.

There were ethers, aldehydes, acids, lactones, furane derivatives, and terpenes in the composition of volatile compounds in strawberry juices. Acids—60.1% and furanone—28.9% from the total amount of juice volatiles had a large share among aromatic juice compounds. Among the total amount of volatile compounds, a large share belonged to 2,5-dimethyl-4-methoxy-3(2H)-furanone (mesifurane) (21% of the total sum of juice volatiles), linoleic acid (16.6%), trans-cinnamic acid (16.0%), palmitoleic acid (9.5%), 2.5-dimethyl-4-oxy-3(2H)-furanone (6.7%), hexanoic (caproic) acid (6.2%), 2-ethyl hexanoic (capronic) acid (4.8%). Furfural was found among volatile compounds of natural unclarified strawberry juice; it was identified earlier in other processed strawberry products and this confirms the features of non-fermentative darkening of the product.

Ethyl butanoate in the amount of 1.2% from the total content of volatile compounds and isoamyl butanoate—1.4% were identified among ethers in a strawberry juice. The share of each other ether found in a juice is at the level of 0.1–0.6%. The aldehyde content does not exceed 0.5%. Also, 2H-pyran-2,6(3H)-dion, the share of which was 1.7% of the total sum of volatile compounds, was identified, which confirms Mayar's reaction.

Terpene compounds of a natural strawberry unclarified juice include linalool (0.4% from the total sum of volatiles), α-terpineol (0.3%) that add spicy scents to juice aroma, and oxydebisabolol A (0.9%), oxydebisabolol B (0.5%), nerolidol (0.8%) which add sweet flower scents [5].

The aroma of strawberry jams is formed under the effect of acids, alcohols, and ethers [39, 40], which can be both of natural origin and the result of heat treatment. Acids add a lot to the aroma of jams: 2-methylbutyric acid, hexanoic (caproic) acid, octadecanoic acid, dodecanoic acid, tetradecanoic acid, palmitoleic acid, trans-cinnamic acid; alcohols: 1-hexanol, 3-methyl-3-buten-2-ol, linalool, linalool oxide, α-terpineol, trans-nerolidol, benzyl alcohol [39].

As a result of high-temperature treatment, sugar caramelization, and Mayar's reaction, strawberry products obtain boiled, burnt, and caramel tastes [29, 41–43].

Contrary to this, green fruit scents which are typical for fresh berries are less pronounced [2, 30]. High concentrations of furaneols add characteristic caramel and sweet scents to the aroma of strawberry jams [29, 43].

According to Lambert et al. [17], the sterilization of strawberry puree with juice at 120°C for 20 min causes serious losses of flower aromas along with the formation of geraniol and vanillin. In addition, the concentration of butylacetate increases by 1.7 times, 2-Hexen-1-al—by 3.2, butyric acid—by 2, 2-methylbutanoic acid—by 1.6, hexanoic acid—by 1.8, furaneol—by 3.0, nerolidol—1.7, octanoic acid—by 1.7 and γ-decalactone—by 1.5 times, as compared with fresh strawberries.

The main volatile compounds of strawberry jams belong to the classes of acids, alcohols, and ethers [39, 40] and they are both of natural origin and can be the result of heat treatment. The most common among acids are 2-Methylbutyric acid, hexanoic acid, octanoic acid, dodecanoic acid, tetradecanoic acid, palmitoleic acid, trans-cinnamic acid. The most common alcohols are 1-hexanol, 3-methyl-3-buten-2-ol, linalool, cis-epoxy-linalool, cis-Linalool oxide, α-Terpineol, trans-nerolidol, benzyl alcohol. Active compounds include ethyl butanoate, methyl and ethyl-capronates, 3-Hydroxybutanoic acid methyl ester, and 3-Hydroxy hexanoic acid methylester [43].

Thirty-eight components, including esters, aldehydes, ketones, furanone, acids, aromatic compounds, lactones, and terpene compounds, were identified in the composition of volatiles of strawberry jams made of cultivars Polka, Ducat, and Honey. The most meaningful shares are: acids—65.6–76.8%, furanes—8.3–14.6% and aldehydes—3.4–10.8%. The share of esters in jams exceeds 0.7–3.1% of the total volatile content. It is important to mention that in strawberry jams made of Polka cultivar the share of esters and aldehydes is much higher: 3.1 and 10.8%, that of furanes and acids, on the contrary, is the lowest—8.3 and 65.6% which proves strong expression of scents typical for fresh strawberries.

Characteristic compounds for strawberry jam flavor made of the studied cultivars are hexanoic (caproic) acid (0.84–6.89 mg/kg), which is 6.9–22.9% of the total volatile amount depending on their quantity for each cultivar, hexadecanoic acid (2.5–12.4%), 2-ethyl hexanoic (capronic) acid (3.1–10.7%), trans-cinnamic acid (17.5–25.3%), linoleic acid (0.3–7.2%), furil hydroxy methylketone (3.1–6.0%), 2,5-dimethyl-4-methoxy-3(2H)-furanone (mesifurane) (7.4–13.7%), furfural (0.8–3.1%), 5-hydroxymethylfurfural (0.8–5.2%), vanillin (0.2–0.8%) [5].

The availability of furfural (0.8–3.1%), 5-hydroxymethylfurfural (0.8–5.2%) 5-methylfurfural (0.7%) in strawberry jams indicates non-fermentative darkening during thermal treatment [39, 40].

Small amounts of 2H-pyran-2,6(3H)-dion and 3,5-hydroxy-2-dimethyl-4H-pyran-4—(0.09–0.66 mg/kg) which, depending on the cultivar, is 0.5–0.9% of the total volatile content in jams, were found; and according to [39] they are the products of Maiyar reaction resulted from the reaction of glucose with glutamic acid, glycine, butylamine, lysine, hydroxyproline and/or phenylalanine (amino acids) [5].

Terpenic compounds of strawberry jams are presented by small amounts of limonene (0.1 mg/kg, which is 0.8%) and α-terpineol (0.2–1.3%), they were found in fresh berries [16] these compounds add aromatic scent to fresh berries [15, 16]; oxyde bisabolol A (0.1–0.3%), trans-linalool oxide (0.1–0.3%), cis-linalool oxide (0.3%), however no data concerning their presence in fresh strawberries is available.

3. Conclusions

Thus, the aroma of fresh strawberries is developed during ripening and it depends on the environmental conditions, a strawberry cultivar, a degree of maturity, and post-harvest conditions. The aroma of strawberries consists of a complex mixture of compounds including ethers, aldehydes, alcohols, ketones, lactones, furanone, and terpene compounds. Refrigerating, freezing, and heat treatment of berries have an impact on the change of aroma. The understanding of the nature of these changes will make it possible to predict the quality of the refrigerated berries and the canned output.

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