Food Research International 160 (2022) 111694

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Impact of Zulla cover crop in vineyard on the musts volatile profile of *Vitis vinifera* L. cv Syrah

E. Valero [a], F. Arranz [b], B.J. Moyá [b], S. Cruz [c], B. Puertas [c], M.L. Morales [b,*]

[a] Área de Nutrición y Bromatología, Dpto. Biología Molecular e Ingeniería Bioquímica, Univ. Pablo de Olavide, Sevilla, España
[b] Área de Nutrición y Bromatología, Dpto. Nutrición y Bromatología, Toxicología y Medicina Legal, Fac. Farmacia, Univ. Sevilla, Sevilla, España
[c] Instituto de Investigación y Formación Agraria y Pesquera (IFAPA), Rancho de la Merced, 11471 Jerez de la Frontera, España

ARTICLE INFO

Keywords:
Cover crop
Soil tillage
Organic cultivation
Grape must
Volatile compounds
Hedysarum coronarium L.
Warm climate

ABSTRACT

Grape aromatic characteristics are very important for producing quality wines. There have been very few studies on concentrations of volatile compounds in grape berries from vines with cover crops. For this reason, the aim of this work was to evaluate the influence of "Zulla" cover crop on the volatile profiles of organically grown Syrah variety grapes. For this purpose, volatile profiles of grapes obtained from vines with three different amounts of cover crop (one line, two lines, and four lines) and without cover crop, over three harvests (2019, 2020, and 2021) were determined. Moreover, a comparative study of conventional and organic crops, both submitted to soil tillage, was performed. The grape samples came from a warm climate zone. Must volatile compounds were determined by sequential sorptive extraction with Twisters by immersion (SBSE) and headspace (HSSE), followed by GC–MS analysis. A total of 160 compounds were determined and most of them were influenced by the presence of cover crop. However, the results showed an important influence of the harvest year over agronomic practices. Therefore, organic cultivation using Zulla cover crop seems to be a suitable tool for the implementation of friendly ecosystem management in a warm climate Syrah vineyard.

1. Introduction

There is important world interest in increasing organic farming to guarantee environmental sustainability and biodiversity, among other positive effects. In 2019, Spain was the country with the largest number of hectares of organic vineyards worldwide (27% of the world's organic vineyard area) (OIV, 2021). In this kind of cultivation, herbicides cannot be used to prevent the growth of vegetation between rows of vines. Thus, tilling the soil is the most widespread agronomic practice used to keep the ground free from vegetation. However, this soil management strategy favours soil erosion and alters its microbiota (Abad, Marín, Santesteban, Cibriain, & Sagüés, 2020). As an alternative, the use of cover cropping is proposed in organic vineyards, which implies benefits for soil quality, but it could also reduce the availability of nutrients and water for the vine (Bouzas-Cid, Trigo-Córdoba, Orriols, Falqué, & Mirás-Avalos, 2018), influencing the canopy vigour and consequently the must quality. The kinds of plants most used as cover crops in vineyards are grasses and legumes (Abad, de Mendoza, Marín, Orcaray, & Gonzaga Santesteban, 2021). The former provides organic material, and the latter increase the soil nitrogen.

Wine organoleptic characteristics such as colour, aroma, and taste drive their purchase by the consumer. Wine aroma is constituted by a wide variety of volatile compounds with different origins, directly deriving from grape (i.e., varietal or primary aromas), or formed during fermentation and post-fermentation steps (Antalick et al., 2015; Morales, Fierro-Risco, Ríos-Reina, Ubeda, & Paneque, 2019; Ribéreau-Gayon, Glories, Maujean, & Dubourdieu, 2006).

With respect to the varietal aroma, in addition to depending on the grape variety, this could be affected by many other factors, such as sunlight radiation, water deficit, temperature, or soil management, among others (Alem, Rigou, Schneider, Ojeda, & Torregrosa, 2019; Coletta et al., 2021).

Among red grape varieties, Syrah is one grape variety cultivated in many countries (31) and, in 2015, its vineyard area was 190,000 ha. In Spain, the percentage of cultivation is still low, occupying 2.1% of the total of vineyard ha (OIV, 2017). Its cultivation is easy, despite the fact that it requires a lot of hours of sunshine and medium–high temperatures. It is a type of grape that resists most of the diseases that affect other varieties. Syrah is used to produce monovarietal as well as blended wines. They are very pleasant, balanced and structured wines,

* Corresponding author.
E-mail address: mlmorales@us.es (M.L. Morales).

https://doi.org/10.1016/j.foodres.2022.111694
Received 31 March 2022; Received in revised form 6 July 2022; Accepted 12 July 2022
Available online 14 July 2022

characterised by an intense red colour and fruity aromas (predominantly forest fruits) (Peñín & Diez, 1997).

There have been very few studies of the effect of vineyard cover crops on the volatile profile of grapes and controversial results have been obtained. On one hand, Xi, Tao, Zhang, and Li (2011) studied the influence of permanent green cover crops on Cabernet Sauvignon vines from northwest China. They concluded that wines from cover crops had higher contents of volatile compounds, thus, this agronomic practice could enhance the wine content of aroma compounds. On the other hand, Coletta et al. (2021) researched the effect of cover crops on the Negroamaro grape variety from southern Italy and they observed that soil tillage treatment favoured the concentrations of free volatile versus cover crop treatment. More recently, Bouzas-Cid et al. (2018) evaluated permanent cover crops on the volatile profile of wines from the Mencía variety grape grown in northwest Spain. These researchers concluded that this practice slightly influenced the concentrations of volatiles in the studied wines, therefore, the wine aroma might be modulated using cover crops in humid climates. Then, the use of cover crops may produce different effects, depending on grape variety, climate, the kind of cover crop, and its management. Consequently, its use should be evaluated for each grape variety, climate, and agronomic condition.

The use of cover crops may also contribute to preserving plant biodiversity, therefore, the use as cover crop of plants from wild autochthonous flora should be encouraged, since these also have the advantage of being adapted to the local climate.

Different assays of cover crops with Syrah vines have been performed, using *Medicago truncatula, Medicago rigidula, Medicago polymorpha* and spontaneous crops (Kazakou et al., 2016), *Medicago truncatula, M. rigidula,* and *M. polymorpha* (Guilpart, Roux, Gary, & Metay, 2017), *Festuca rubra* (Delpuech & Metay, 2018), *Bromus hordeaceus* and *Secale cereal* (Linares Torres, De La Fuente Lloreda, Junquera Gonzalez, Lissarrague Garcia-Gutierrez, & Baeza Trujillo, 2018). In these works, several parameters have been studied, such as grape and vine yield, vine leaf water potential, assimilable nitrogen in grapes, or disease susceptibility. However, to our knowledge, the extent to which a cover crop influences the volatile composition of Syrah grape is yet to be studied.

The aim of this work was to study, for the first time, the effect of organic cultivation and different amounts of Zulla cover crop on the free volatile compounds of Syrah grapes grown in warm climates. Moreover, a comparative study of conventional and organic crops, both submitted to soil tillage, was performed. Zulla (*Hedysarum coronarium L.*) is a wild legume originated from the Mediterranean basin (Tava et al., 2021). This plant grows spontaneously in the study area, therefore, its use will contribute to biodiversity maintenance. To our knowledge, this wild plant has not been used as a vineyard cover crop. Although major studies about the effects of agronomic factors have been performed by analysing the wines, in our work the volatile composition was directly determined in must samples, since the alcoholic fermentation factors have a significant influence on the volatile profile of the resulting wines, which makes it difficult to have a clear idea of which changes are due to agronomic factors.

2. Materials and methods

2.1. Samples

This study was performed during three consecutive vintages, 2019, 2020, and 2021. in two vineyards (conventional and organic), with *Vitis vinifera* L. cv Syrah grapevine. Vineyards were located in the IFAPA Centre "Rancho de La Merced", in the Jerez winegrowing region, Spain (36:45:29 N, 06:00:58 W, 35 m altitude), in an area with limestone soil composed of 19% sand, 38.5% clay, and 42.5% silt. The distance between the two vineyards was 2 Km and both are included in region V according to climatic classification of viticultural regions by Amerine and Winkler (1944). Climatological data was taken from the vineyard weather station, and shown in Fig. 1S. (A and B). In both the conventional and organic vineyards, the rootstock of vines was 140 Ru., and the vines were trained on the trellis system of three wire and winter pruning was double cordon, with 2 arms, 3 spurs per arm and 2 buds per spur. That is, a load of 12 buds per vine. The grapes were harvested manually. A vineyard with bare soil by tillage was used as a control. No irrigation was performed in the vineyards.

The conventional vineyard was treated with agricultural chemicals, such as gliphosate 25%, difluphenican 6,25% and metribuzin 25% at the rate of 4 L/Ha as herbicide, and different treatments were applied, such as insecticide, nematicide and fungicide, at four different times and doses, between March and June. All products were applied either around or directly onto the grape vines. The organic vineyard was treated only with micronised sulfur (98.5% sulfur, DP. Afepasa) at the rate of 30 kg/Ha, and copper oxychloride 70% (Oxirame 70, Naturdai) as fungicide.

Zulla (*Hedysarum coronarium* L.) cover crops were planted (20 Kg/Ha) in lanes 4, 5, 10, 11, 14, 15, 16, and 17 (Fig. 2S, supplementary material), in October 2018 and were maintained until March 2019. At this time, it was cleared and a week later the lanes were tilled to avoid the cover ground competing with the vineyard. In the second and third years (2019–20 and 2020–21), the cover crop was allowed to grow spontaneously, with no new planting of Zulla, and the same process of clearing and soil tillage was carried out.

In order to evaluate the volatile composition of musts, three sampling campaigns were performed. Bunches were always collected from the same plant at a similar maturation stage (approx. 24 °Brix). With the present experimental design, 15 grape samples were collected every year, 12 grape samples in the organic vineyard (SE), for every cover crop density (3 samples for every different density) and 3 grape samples in the conventional vineyard (SC). The different cover crop densities evaluated were cover crop on one side and tillage on the other side of the row (LZ), cover crop on both sides of the row (ZZ), cover crop on two rows on both sides of the sampled row (4Z) and tillage on both sides of the vine row as a control (LL). Approximately 2 kg of grapes, stems included, were harvested in aseptic conditions from each sampling point and placed directly into sterile bags, which were transported to the laboratory in portable refrigerators with plastic ice blocks. At the laboratory, grapes were squeezed by hand in the plastic bags, opened and about 50 mL of juice was poured into a glass vial for further volatile compounds analyses.

2.2. Determination of volatile compounds in musts by SBSE-HSSE-GC-MS

The musts' volatile fraction was extracted by a sequential sorptive extraction with polydimethylsiloxane Twisters®. Two Twisters® were used for each sample. The two steps of the sequential extraction procedure were, first, an extraction in immersion (SBSE), followed by an extraction in headspace (HSSE) (Ubeda, Callejón, Troncoso, Peña-Neira, & Morales, 2016). 7.5 mL of must were placed into a 20 mL vial, plus 10 μL of the internal standard (4-methyl-2-pentanol, 1044 mg/L) and 2.25 gr of NaCl. For the sequential extraction procedure, a Twister® was immersed in the sample using a Twicester® device for 1 h, at room temperature, while the sample was stirred with a conventional magnetic stir bar at 200 rpm. Subsequently, the twister was removed with tweezers, rinsed with Milli-Q water, dried with lint-free tissue paper and reserved in a tightly closed 2 mL vial. Then, another twister was placed in an open glass insert inside the vial and the sample was heated in a water bath at 62 °C for 1 h. The twister was removed from the vial, and we proceeded in the same way as mentioned above. Both twisters were then introduced into the same desorption tube and simultaneously desorbed. The analytical equipment, desorption conditions, and GC–MS used are detailed in Ubeda et al. (2016).

Compounds were identified using mass spectra matching the NIST/EPA/NIH Mass Spectral Library (NIST 17) and the linear retention index (LRI) of authentic reference standards. LRIs were calculated by injecting

n-alkanes mixture (C10–C40) under conditions identical to those of the samples.

Subsequently, we considered the identification of a compound confirmed when the mass spectrum and LRI values matched those of the standards. The identification of a compound was considered tentatively (TI) when its mass spectrum matched that of the NIST mass spectral library and its LRI value that of the literature. For the remaining compounds, of which only their mass spectrum matched that of the NIST library, their identification cannot be confirmed, furthermore, among these we call unknown compounds (n.i.) the compounds that had low values of probability of right identification in the search results in the NIST library.

2.3. Statistical analyses

The values of relative peak area of the diverse VOCs found in each agronomic treatment were subjected to analysis of variance (ANOVA) (Fisher's LSD post hoc test) using INFOSTAT software (FCA, Universidad Nacional de Córdoba, Argentina). The possible existence of correlations between an abundance of Zulla and volatile compounds was also studied by regression analysis. The multivariant statistical analysis performed was principal component analysis (PCA). These last two analyses were performed using Statsoft Statistical, version 7.0 (Statsoft, Tulsa, OK). Heatmap visualisation of cluster analysis was performed using the MetaboAnalyst 4.0 (web interface) (Chong & Xia, 2018).

3. Results and discussion

A total of 160 volatile compounds were detected by a sequential extraction procedure SBSE-HSSE followed by TD-GC-MS analysis in free fractions from Syrah musts. The total number of compounds detected in each harvest was different, ranging from 123 in the 2020 harvest and 156 in the 2019 harvest. Eighty-two of them were positively identified by mass spectrum according to the mass spectral database and standard LRI and 39 tentatively identified (TI) by mass spectrum and LRI according to data found in the literature. Results were expressed as relative peak area values with respect to IS and are shown in Table 1, classified according to their functional groups. Alcohols, aldehydes, and ketones were the main volatile compounds identified in the three harvests.

The highest total content of volatile compounds was observed in musts from 2019 for most of the different cultivation conditions studied. There were several compounds detected only in one harvest, we can highlight veratrol in 2019, an aldehyde tentatively identified as safranal in 2020, and heptanal in the 2021 harvest, among others. Veratrol (1,2-dimethoxybenzene) is a volatile compound related to insect attraction (Dötterl & Jurgens, 2005), it was detected in female inflorescences of wild grapevine (Zito, Scrima, Sajeva, Carimi, & Dötterl, 2016).

Conversely, rotundone, a sesquiterpene compound characteristic of the Syrah grape variety from cool climates (Wood et al., 2008), was not detected as expected.

In order to discuss the results of this work, first of all, we are going to contrast the musts' volatile composition from conventional and organic cultivation, both subjected to soil tillage, and subsequently, the organic musts' volatile composition from vines cultivated with different proportions of Zulla covert crop.

3.1. Conventional crop versus organic crop

The volatile composition of musts from the Syrah grape variety obtained from conventional and organic cultivation during three harvests was compared. Considering jointly the results of the three harvests, we observed similar trends in the total content of aldehydes, nitrogen compounds, and C_{13}-norisoprenoinds, which were higher in organic than in conventional cultivation. The differences were significant in the case of total content of nitrogen compounds and C_{13}-norisoprenoinds. Among compounds detected in the three harvests, 19 of them presented higher contents in musts from organic than in conventional cultivation. Besides, the differences were significant for 1-nonanol, 2-heptenal, *trans*, *cis*-2,4-heptadienal, *trans*-2-nonenal, 2,3-octanedione, 6-methyl-5-hepten-2-one, 4-methyl-5H-furan-2-one, γ-decalactone, β-damascenone, *cis*-linalool oxide, hotrienol, epoxylinalol, and the unknown compound n.i. (*m/z* 70-55-43). These compounds provide herbaceous, floral, and fruity aromas. Conversely only three compounds were more abundant in musts from conventional cultivation than in organic musts, namely benzyl alcohol, 2,4-hexadienal isomers, and 4-methyl-2-hexanone, the differences only being significant for the last.

However, if we considered each harvest independently, the volatile compound total content followed similar trends in both the 2019 and 2020 harvests, being higher in musts from organic than in conventional cultivation, although it was only statistically significant for the 2019 harvest. In the 2021 harvest, both kinds of musts presented a very similar volatile compound total content. The total content of nitrogen compounds was the only case in which we observed a significantly higher amount in organic than in conventional musts for every harvest studied. In the case of aldehydes and C_{13}-norisoprenoinds total contents, organic musts also presented higher amounts, but significant differences between the two kinds of cultivations were only observed in the 2021 harvest. For the remaining chemical groups, in most cases, the total contents were higher in musts from organic cultivation for the 2019 and 2020 harvests and in musts from conventional cultivation for the 2021 harvest. Among them, we can highlight the case of acetic acid esters, ketones, lactones, methyl esters and other esters groups which showed significantly different results for the three harvests (Fig. 3S).

Regarding the content of each volatile compound from the major chemical groups, alcohols, aldehydes, and ketones, we observed significantly different amounts for most of them, depending on the kind of cultivation. These amounts were higher in organic than conventional musts in 2019 and 2020 and contrariwise in the 2021 harvest for most of them. In the case of alcohols, 1-hexanol, *trans*-3-hexanol, *cis*-3-hexen-1-ol, *trans*-2-hexen-1-ol, and *cis*-2-hexen-1-ol, responsible for herbaceous aroma, and 1-octen-3-ol, 1-heptanol, 2-ethyl-1-hexanol, 1-octanol, *trans*-2-octen-1-ol, and furfuryl alcohol, they were significantly more abundant in organic musts in the 2019 and 2020 harvests and in musts from conventional cultivation in the 2021 harvest. In the case of furanic aldehydes (2-furfuraldehyde, 5-methyl-2-furfuraldehyde, 5-hydroxymethylfurfural, and 3-furfuraldehyde), the same trend was observed. The same occurred in the case of ketones such as diacetyl, 1-hydroxy-2-propanone, 1-hydroxy-2-butanone, 2-acetylfuran, 3-methyl-2-cyclopenten-1-one and 2-cyclopentene-1,4-dione, in the case of diacetyl, there was no significant difference between crop types in the 2019 harvest. This also occurred in other minor chemical groups such as the group of acids.

However, 2-heptanal, *trans*-2-nonenal, and nonanal were significantly more abundant in organic musts in the three harvests (with the exception of nonanal in the last harvest). These compounds provided herbaceous and fatty or waxy aromas. Regarding ketones, the contents were higher in organic musts in the three harvests for 2,6-dimethyl-4-heptanone and 6-methyl-5-hepten-2-one, with chemical and citric aromatic notes, respectively.

Moreover, a higher number of terpenes were significantly more abundant in organic than in conventional musts in each harvest, with a similar trend in the three harvests only in the case of *cis*-linalool oxide. When they studied the evolution of free terpenes in several grape varieties, Luo et al. (2019), also found differences between harvests.

Although there were few samples, a PCA considering the volatile profile of musts from conventional and organic cultivation of the three harvests was performed. The first three PCs explained 81.8 % of the total variance of the data. As can be seen in Fig. 1, PC1 separated the samples of the 2019 harvest from those of the other two harvests and PC2 separated the samples of the 2020 and 2021 harvests. The musts from vines cultivated using the conventional method were located closer to each other than those from organic cultivation. If we consider PC3, this

Table 1
Volatile profiles of grape musts from vines submitted to different agronomic conditions in three consecutives harvests.

		Relative peak area* ± SD†					
Volatile Compounds	ID	Harvest	SC	SELL	SELZ	SEZZ	SE4Z
Acids							
Acetic acid	A	19	0.0049 ± 0.0010^{a}	0.0098 ± 0.0012^{b}	0.00301 ± 0.00016^{a}	0.00966 ± 0.00014^{b}	0.0098 ± 0.0010^{b}
		20	0.0071 ± 0.0008^{c}	0.0090 ± 0.0010^{d}	0.00392 ± 0.00005^{a}	0.0052 ± 0.0004^{b}	0.00415 ± 0.00007^{a}
		21	0.0146 ± 0.0013^{c}	0.0038 ± 0.0005^{b}	0.00189 ± 0.00013^{a}	–	–
Propanoic acid	A	19	–	0.00243 ± 0.00005^{a,b}	–	0.00238 ± 0.00015^{a}	0.0028 ± 0.0003^{b}
		20	–	–	–	–	–
		21	–	–	–	–	–
Hexanoic acid	A	19	0.0086 ± 0.0013^{a}	0.023 ± 0.003^{b}	0.0036 ± 0.0005^{a}	0.0226 ± 0.0019^{b}	0.036 ± 0.003^{c}
		20	0.00212 ± 0.00018^{a}	0.0049 ± 0.0007^{b}	0.0112 ± 0.0015^{c}	0.0049 ± 0.0004^{b}	0.0042 ± 0.0004^{b}
		21	0.0031 ± 0.0005	–	–	–	–
2-Ethylhexanoic acid	B	19	0.0022 ± 0.0005^{a,b}	0.0048 ± 0.0007^{c}	0.00131 ± 0.00023^{a}	0.00245 ± 0.00019^{a,b}	0.00425 ± 0.00017^{b,c}
		20	–	–	0.0022 ± 0.0004^{a,b}	0.0019 ± 0.0004^{a,b}	0.0017 ± 0.0002^{b}
		21	–	–	–	–	–
Total of acids		19	0.016 ± 0.007^{a}	0.041 ± 0.003^{b}	0.0079 ± 0.0004^{a}	0.0371 ± 0.0021^{b}	0.0532 ± 0.0017^{c}
		20	0.0092 ± 0.0009^{b}	0.01391 ± 0.00019^{a,b}	0.0173 ± 0.0019^{a}	0.0120 ± 0.003^{a,b}	0.010 ± 0.006^{a,b}
		21	0.0177 ± 0.0008^{a}	0.0038 ± 0.0005^{b}	0.00189 ± 0.00013^{c}	–	–
Acetic Acid Esters							
Methyl acetate	A	19	0.0069 ± 0.0009^{a}	0.028 ± 0.003^{c}	0.0156 ± 0.0016^{b}	0.040 ± 0.004^{d}	0.0482 ± 0.0006^{e}
		20	0.0111 ± 0.0015^{a}	0.0162 ± 0.003^{b}	0.037 ± 0.003^{e}	0.020 ± 0.003^{c}	0.0265 ± 0.0021^{d}
		21	0.00191 ± 0.00019^{a}	0.00128 ± 0.00019^{a}	0.0085 ± 0.0013^{b}	0.0208 ± 0.0003^{d}	0.0169 ± 0.0024^{c}
Ethyl acetate	A	19	0.027 ± 0.004^{a,b}	0.054 ± 0.008^{b}	0.00807 ± 0.0012^{a}	0.0042 ± 0.0006^{a}	0.0243 ± 0.0013^{a,b}
		20	0.0110 ± 0.0005^{a}	0.036 ± 0.004^{b}	0.028 ± 0.004^{b,c}	0.0179 ± 0.0011^{a}	0.0268 ± 0.0004^{b}
		21	0.023 ± 0.003^{c}	0.0056 ± 0.0004^{a}	0.00449 ± 0.00016^{a}	0.0081 ± 0.0012^{a}	0.0154 ± 0.0013^{b}
Butyl acetate	A	19	–	0.00122 ± 0.00011^{b}	0.00071 ± 0.00002^{a}	–	–
		20	–	–	–	–	–
		21	–	–	–	–	–
Hexyl acetate	A	19	0.0027 ± 0.0003^{a,b}	0.0049 ± 0.0003^{d}	0.00349 ± 0.00010^{c}	0.003199 ± 0.000006^{b,c}	0.00243 ± 0.00007^{a}
		20	0.0039 ± 0.0004^{a}	0.0074 ± 0.0008^{d}	0.0056 ± 0.0006^{c}	0.00496 ± 0.00011^{b}	0.005358 ± 0.000005^{b,c}
		21	–	–	–	–	–
cis-3-hexenyl acetate	A	19	0.0034 ± 0.0003^{d}	0.00102 ± 0.00009^{a}	0.00148 ± 0.00021^{b,c}	0.00186 ± 0.00005^{c}	0.00109 ± 0.00007^{a,b}
		20	0.00195 ± 0.00005^{b}	–	0.00231 ± 0.00013^{c}	0.0025 ± 0.0006^{d}	0.00140 ± 0.00007^{a}
		21	–	–	–	–	–
2-Hexenyl acetate	B	19	0.00262 ± 0.00021^{a,b}	0.0032 ± 0.0004^{b}	0.0048 ± 0.0007^{c}	0.00154 ± 0.00023^{a}	0.0049 ± 0.0003^{b}
		20	–	0.00300 ± 0.00016^{c}	0.00161 ± 0.00019^{a}	0.00197 ± 0.00012^{b}	0.00169 ± 0.00011^{a}
		21	–	–	–	–	–
2-Phenylethyl acetate	B	19	0.00096 ± 0.00004^{b}	0.001214 ± 0.000013^{c}	0.00063 ± 0.00009^{a}	0.00106 ± 0.00013^{b,c}	0.00091 ± 0.00011^{b}
		20	–	–	–	–	–
		21	–	–	–	–	–
Total of acetic acid esters		19	0.044 ± 0.017^{b}	0.094 ± 0.019^{a}	0.0348 ± 0.0012^{b}	0.0514 ± 0.0014^{b}	0.082 ± 0.003^{a}
		20	0.0279 ± 0.023^{c}	0.0620 ± 0.0004^{a}	0.074 ± 0.011^{a}	0.047 ± 0.003^{b}	0.0618 ± 0.0018^{a}
		21	0.025 ± 0.003^{b}	0.00685 ± 0.00016^{d}	0.0130 ± 0.0014^{c}	0.0289 ± 0.0015^{a,b}	0.03 ± 0.04^{a}
Alcohols							
Methanol	A	19	0.062 ± 0.009^{a}	0.065 ± 0.007^{a}	0.25 ± 0.04^{b}	0.045 ± 0.006^{a}	0.082 ± 0.012^{a}
		20	0.095 ± 0.003^{d}	0.034 ± 0.005^{b}	0.134 ± 0.012^{e}	0.046 ± 0.010^{c}	0.0220 ± 0.0008^{a}
		21	0.0107 ± 0.0003^{a}	0.0064 ± 0.0007^{a}	0.029 ± 0.004^{b}	0.035 ± 0.005^{b}	0.06746 ± 0.00016^{c}
Isobutanol	A	19	0.0078 ± 0.0008^{a}	0.024 ± 0.003^{b}	0.00888 ± 0.00005^{a}	0.013 ± 0.003^{a}	0.0084 ± 0.0013^{a}
		20	0.00147 ± 0.00004^{a}	0.0060 ± 0.0010^{a}	0.006 ± 0.003^{a}	0.00395 ± 0.00019^{a}	0.022 ± 0.008^{b}
		21	–	–	–	–	–
1-Butanol	A	19	0.018 ± 0.003^{a}	0.0181 ± 0.0005^{a}	0.011 ± 0.0004^{b}	0.0097 ± 0.0003^{b}	0.0179 ± 0.0018^{b}
		20	0.0114 ± 0.0014^{b}	0.0147 ± 0.0022^{c}	0.006 ± 0.0006^{a}	0.0175 ± 0.0005^{d}	0.0170 ± 0.0017^{d}
		21	0.0234 ± 0.0008^{d}	0.00880 ± 0.00019^{b}	0.0058 ± 0.0006^{a}	0.0083 ± 0.0004^{b}	0.0127 ± 0.0005^{c}
1-Penten-3-ol	B	19	0.0167 ± 0.0004^{b,c}	0.010 ± 0.003^{a}	0.0089 ± 0.0020^{a,b}	0.0146 ± 0.003^{c}	0.016 ± 0.003^{c}
		20	0.0143 ± 0.0011^{a}	0.026 ± 0.003^{c}	0.024 ± 0.003^{c}	0.01969 ± 0.00003^{b}	0.020 ± 0.003^{b}
		21	0.0109 ± 0.0004^{b}	0.0109 ± 0.0009^{b}	0.0095 ± 0.0006^{a,b}	0.0084 ± 0.0006^{a}	0.0105 ± 0.0006^{b}
2-Methyl-1-butanol	A	19	0.0072 ± 0.0011^{b,c}	0.0109 ± 0.0022^{c}	–	0.00449 ± 0.00022^{a,b}	0.0067 ± 0.0004^{b,c}
		20	–	–	–	–	–
		21	0.00346 ± 0.00004	–	–	–	–
3-Methyl-1-butanol	A	19	0.02702 ± 0.00023^{a,b}	0.042 ± 0.006^{b}	0.0170 ± 0.0003^{a}	0.021 ± 0.003^{a}	0.021 ± 0.003^{a}
		20	–	0.084 ± 0.013^{c}	0.0472 ± 0.0014^{a}	0.043 ± 0.006^{a}	0.0620 ± 0.0024^{b}

(*continued on next page*)

Table 1 (*continued*)

		Relative peak area* ± SD†					
Volatile Compounds	ID	Harvest	SC	SELL	SELZ	SEZZ	SE4Z
		21	0.0179 ± 0.0018^{c}	0.0032 ± 0.0005^{a}	0.0044 ± 0.0005^{a}	0.0103 ± 0.0014^{b}	0.0087 ± 0.0011^{b}
2-Hexanol	B	19	0.004446 ± 0.000024^{a}	0.005144 ± 0.000009^{c}	0.00430 ± 0.00014^{a}	0.004827 ± 0.000015^{b}	0.004301 ± 0.000017^{a}
		20	0.006171 ± 0.000013^{c}	0.00596 ± 0.00006^{b}	0.0054 ± 0.0003^{a}	0.00540 ± 0.00011^{a}	0.00553 ± 0.00003^{a}
		21	0.00539 ± 0.00005^{a}	0.0054 ± 0.0003^{a}	0.00523 ± 0.00012^{a}	0.005434 ± 0.000003^{a}	0.00509 ± 0.00003^{a}
5-Methyl-3-hexanol	C	19	0.00473 ± 0.00009	–	–	–	–
		20	0.00584 ± 0.00020^{a}	0.006129 ± 0.000012^{b}	0.00633 ± 0.00015^{b,c}	0.0065 ± 0.0003^{c}	0.00620 ± 0.00009^{b}
		21	0.00481 ± 0.00006^{a}	0.00524 ± 0.00014^{b}	0.00541 ± 0.00005^{b}	0.00541 ± 0.00016^{b}	0.00522 ± 0.00013^{b}
1-Hexen-3-ol	B	19	–	0.00149 ± 0.00020^{a}	0.00245 ± 0.00015^{b}	0.00172 ± 0.00025^{a}	0.00152 ± 0.00019^{a}
		20	0.017 ± 0.003^{c}	0.0083 ± 0.0002^{b}	0.0027 ± 0.0003^{a}	0.0093 ± 0.0007^{b}	0.0040 ± 0.0006^{a}
		21	–	–	–	–	–
1-Pentanol	B	19	0.0102 ± 0.0012^{c}	0.00710 ± 0.00012^{b}	0.0046 ± 0.0004^{a}	0.00533 ± 0.00008^{a}	0.0075 ± 0.0008^{b}
		20	0.0063 ± 0.0004^{a}	0.0096 ± 0.0006^{b}	0.0110 ± 0.0011^{c}	0.00615 ± 0.00005^{a}	0.0100 ± 0.0006^{b}
		21	0.0096 ± 0.0004^{a}	0.0166 ± 0.0024^{b}	0.0090 ± 0.0005^{a}	0.0089 ± 0.0004^{a}	0.0099 ± 0.0003^{a}
cis-2-Penten-1-ol	B	19	0.0167 ± 0.0019^{b}	0.0096 ± 0.0005^{a}	0.0089 ± 0.0012^{a}	0.0146 ± 0.0011^{b}	0.0159 ± 0.0017^{b}
		20	0.0069 ± 0.0003^{a}	0.011326 ± 0.000015^{d}	0.0081 ± 0.0004^{b}	0.0107 ± 0.0006^{c}	0.0114 ± 0.0003^{d}
		21	0.00481 ± 0.00015^{a}	0.0072 ± 0.0011^{b}	0.0046 ± 0.0003^{a}	0.00508 ± 0.00021^{a}	0.00503 ± 0.00002^{a}
2-Heptanol	B	19	0.01567 ± 0.00021^{a}	0.0082 ± 0.0005^{a}	0.0095 ± 0.0007^{a}	0.0084 ± 0.0005^{a}	0.032 ± 0.005^{b}
		20	0.0088 ± 0.0005^{d}	0.01406 ± 0.00004^{e}	0.00566 ± 0.00003^{b}	0.0045 ± 0.0003^{a}	0.0061 ± 0.0004^{c}
		21	0.0057 ± 0.0003^{d}	0.0045 ± 0.0005^{c}	0.00139 ± 0.00019^{a}	0.00210 ± 0.00021^{a}	0.0032 ± 0.0004^{b}
1,2-Butanediol	C	19	0.00105 ± 0.00013^{a}	0.00128 ± 0.00008^{a}	0.00098 ± 0.00007^{a}	0.001010 ± 0.000061^{a}	0.00126 ± 0.00019^{a}
		20	–	0.001998 ± 0.000022^{b}	0.00135 ± 0.00014^{a}	–	–
		21	–	–	–	–	–
1-Hexanol	A	19	3.6 ± 0.4^{a}	4.82 ± 0.18^{b}	3.8 ± 0.4^{a}	3.64 ± 0.18^{a}	3.74 ± 0.11^{a}
		20	3.51 ± 0.03^{a}	4.9 ± 0.6^{c}	5.52 ± 0.11^{d}	4.36 ± 0.11^{b}	4.6 ± 0.4^{b,c}
		21	2.82 ± 0.11^{b}	2.1 ± 0.3^{a}	2.00 ± 0.24^{a}	1.9 ± 0.8^{a}	2.00 ± 0.08^{a}
trans-3-Hexanol	B	19	0.0295 ± 0.0012^{a}	0.02713 ± 0.00021^{a}	0.0361 ± 0.0007^{b}	0.0513 ± 0.0011^{d}	0.044 ± 0.005^{c}
		20	0.0310 ± 0.0021^{a}	0.039 ± 0.003^{c}	0.0357 ± 0.0013^{b}	0.0330 ± 0.0007^{a}	0.0409 ± 0.0021^{c}
		21	0.0153 ± 0.0006^{c}	0.0087 ± 0.0006^{a,b}	0.0074 ± 0.0011^{a}	0.0094 ± 0.0015^{a,b}	0.0101 ± 0.0003^{b}
cis-3-Hexan-1-ol	A	19	0.46 ± 0.07^{a,b}	0.31 ± 0.05^{a}	0.47 ± 0.04^{a,b}	0.73 ± 0.03^{c}	0.53 ± 0.08^{b}
		20	0.21 ± 0.03^{a}	0.23 ± 0.03^{a}	0.433 ± 0.018^{c}	0.419 ± 0.016^{c}	0.268 ± 0.010^{b}
		21	0.1424 ± 0.0018^{c}	0.080 ± 0.008^{a}	0.132 ± 0.008^{b,c}	0.095 ± 0.009^{a}	0.125 ± 0.004^{b}
trans-2-Hexen-1-ol	A	19	3.05 ± 0.14^{a}	3.314 ± 0.019^{a}	3.23 ± 0.21^{a}	2.76 ± 0.07^{a}	3.8 ± 0.6^{a}
		20	2.994 ± 0.004^{a,b}	2.6 ± 0.4^{a}	4.1 ± 0.4^{d}	3.7 ± 0.5^{c}	3.24 ± 0.18^{b}
		21	1.290 ± 0.017^{c}	0.95 ± 0.14^{b}	0.66 ± 0.05^{a}	1.01 ± 0.12^{b}	1.144 ± 0.023^{b,c}
cis-2-Hexen-1-ol	B	19	0.02012 ± 0.00012^{a}	0.0204 ± 0.0008^{a}	0.0307 ± 0.0018^{b}	0.061 ± 0.005^{d}	0.047 ± 0.003^{c}
		20	0.022 ± 0.003^{a}	0.0214 ± 0.0016^{a}	0.0278 ± 0.0006^{b}	0.0224 ± 0.0004^{a}	0.0263 ± 0.0021^{b}
		21	0.006 ± 0.006^{c}	0.00235 ± 0.00023^{a}	0.0031 ± 0.0004^{a,b}	0.0029 ± 0.0002^{a,b}	0.003463 ± 0.000008^{b}
1-Octen-3-ol	A	19	0.0265 ± 0.0008^{a}	0.0332 ± 0.0020^{a,b}	0.063 ± 0.012^{b}	0.035 ± 0.004^{a,b}	0.0502 ± 0.0075^{a,b}
		20	0.0138 ± 0.0014^{a}	0.041 ± 0.004^{c}	0.01539 ± 0.0019^{a}	0.0286 ± 0.0016^{b}	0.030 ± 0.005^{b}
		21	0.027 ± 0.004^{b}	0.0128 ± 0.0017^{a}	0.0153 ± 0.0023^{a}	0.017 ± 0.003^{a}	0.0171 ± 0.0022^{a}
1-Heptanol	A	19	0.0039 ± 0.0003^{a,b}	0.0052 ± 0.0007^{c,d}	0.00311 ± 0.00022^{a}	0.00580 ± 0.00014^{d}	0.0045 ± 0.0004^{b,c}
		20	0.0032 ± 0.0003^{a}	0.0084 ± 0.0012^{c}	0.00460 ± 0.00024^{b}	0.0036 ± 0.0005^{a,b}	0.00408 ± 0.00007^{a,b}
		21	0.00417 ± 0.00020^{c}	0.00232 ± 0.00007^{b}	0.00196 ± 0.00009^{a}	0.00177 ± 0.00009^{a}	0.00195 ± 0.00014^{a}
2-Ethyl-1-hexanol	A	19	0.0135 ± 0.0020^{b}	0.034 ± 0.003^{c}	0.0100 ± 0.0007a,b	0.0109 ± 0.0008^{a,b}	0.00783 ± 0.00007^{a}
		20	0.0203 ± 0.0023^{a}	0.0313 ± 0.0022^{b}	0.0327 ± 0.0018^{b}	0.036 ± 0.003^{c}	0.0312 ± 0.0016^{b}
		21	0.034 ± 0.004^{c}	0.0227 ± 0.0019^{b}	0.018 ± 0.003^{a,b}	0.0136 ± 0.0003^{a}	0.0140 ± 0.0010^{a}
1-Octanol	A	19	0.00347 ± 0.00005^{a}	0.0057 ± 0.0007^{b}	0.00365 ± 0.00017^{a}	0.0037 ± 0.0003^{a}	0.00411 ± 0.00013^{a}
		20	0.00349 ± 0.00004^{a}	0.0095 ± 0.0016^{d}	0.0059 ± 0.0004^{c}	0.00445 ± 0.00014^{a,b}	0.00494 ± 0.00013^{b}
		21	0.00547 ± 0.00017^{b}	0.0035 ± 0.0004^{a}	0.0070 ± 0.0004^{c}	0.0058 ± 0.0008^{b}	0.00396 ± 0.00008^{a}
trans-2-Octen-1-ol	B	19	0.00125 ± 0.00007^{a}	0.00205 ± 0.00018^{b}	0.00137 ± 0.00009^{a}	0.0017 ± 0.0003^{a,b}	0.00145 ± 0.00022^{a,b}
		20	0.00136 ± 0.00011^{a}	0.0043 ± 0.0005^{d}	0.00325 ± 0.00005^{c}	0.00225 ± 0.00013^{b}	0.00318 ± 0.00007^{c}
		21	0.00239 ± 0.00008^{b,c}	0.00175 ± 0.00002^{a}	0.0027 ± 0.0004^{c}	0.00157 ± 0.00021^{a}	0.00191 ± 0.00013^{a,b}
1-Nonanol	B	19	0.00214 ± 0.00021^{a}	0.0053 ± 0.0003^{c}	0.00273 ± 0.00023^{a}	0.0042 ± 0.0006^{b}	0.00356 ± 0.00005^{b}
		20	0.00369 ± 0.00015^{a}	0.0101 ± 0.0015^{d}	0.0066 ± 0.0003^{c}	0.00519 ± 0.00006^{b}	0.0048 ± 0.0004^{b}
		21	0.00409 ± 0.00013^{a}	0.00371 ± 0.00011^{a}	0.0058 ± 0.0003^{b}	0.0056 ± 0.0008^{b}	0.00396 ± 0.00013^{a}
Furfuryl alcohol	A	19	0.056 ± 0.006^{b}	0.0785 ± 0.0009^{c}	0.033 ± 0.003^{a}	0.056 ± 0.004^{b}	0.0570 ± 0.0016^{b}
		20	0.0215 ± 0.0005^{a}	0.062 ± 0.007^{d}	0.0441 ± 0.0003^{c}	0.0386 ± 0.0017^{b}	0.026 ± 0.004^{a}
		21	0.050 ± 0.007^{b}	0.027 ± 0.004^{a}	0.0261 ± 0.0006^{a}	0.028 ± 0.003^{a}	0.0199 ± 0.0019^{a}

(*continued on next page*)

Table 1 (*continued*)

		Relative peak area* ± SD†					
Volatile Compounds	ID	Harvest	SC	SELL	SELZ	SEZZ	SE4Z
1-Decanol	B	19	0.000827 ± 0.000024^{a}	0.00162 ± 0.00008^{b}	0.00097 ± 0.00007^{a}	0.00408 ± 0.00011^{c}	–
		20	–	–	–	–	–
		21	–	–	–	–	–
Benzyl alcohol	A	19	0.029 ± 0.003^{a}	0.0175 ± 0.0007^{a}	0.022 ± 0.003^{a}	0.0314 ± 0.0003^{a,b}	0.041 ± 0.003^{b}
		20	0.0134 ± 0.0018^{d}	0.0072 ± 0.0005^{a}	0.0086 ± 0.0011^{a,b}	0.0096 ± 0.0016^{b,c}	0.0106 ± 0.0014^{c}
		21	0.0144 ± 0.0004^{d}	0.0087 ± 0.0010^{c}	0.00395 ± 0.00022^{a}	0.0061 ± 0.0005^{b}	0.00472 ± 0.00019^{a,b}
2-Phenylethanol	A	19	0.131 ± 0.007^{b,c}	0.087 ± 0.005^{a,b}	0.058 ± 0.009^{a}	0.163 ± 0.010^{c}	0.17 ± 0.03^{c}
		20	0.06285 ± 0.00017^{b}	0.079 ± 0.003^{c}	0.0462 ± 0.0004^{a}	0.041 ± 0.003^{a}	0.070 ± 0.010^{b,c}
		21	0.0401 ± 0.0022^{c}	0.0152 ± 0.0012^{a}	0.01393 ± 0.00011^{a}	0.0176 ± 0.0003^{a,b}	0.022 ± 0.003^{b}
1-Dodecanol	B	19	0.0212 ± 0.0019^{d}	0.0199 ± 0.0024^{c,d}	0.01698 ± 0.00003^{b,c}	0.009819 ± 0.000015^{a}	0.0157 ± 0.0018^{b}
		20	0.00734 ± 0.00004^{a}	0.0060 ± 0.0007^{a}	0.019 ± 0.003^{c}	0.00957 ± 0.00008^{b}	0.0095 ± 0.0013^{b}
		21	0.0129 ± 0.0016^{a}	0.01625 ± 0.00005^{a}	0.0172 ± 0.0021^{a}	0.031 ± 0.005^{b}	0.0127 ± 0.0008^{a}
1-Tridecanol	B	19	0.00107 ± 0.00008^{a}	0.00190 ± 0.00021^{c}	0.00101 ± 0.00008^{a}	0.00128 ± 0.00004^{a,b}	0.00161 ± 0.00015^{b,c}
		20	0.001518 ± 0.000009^{a}	0.0016 ± 0.0003^{a}	0.00221 ± 0.00021^{b}	0.00169 ± 0.00013^{a}	0.00167 ± 0.00023^{a}
		21	0.0017 ± 0.0003^{b}	–	0.00117 ± 0.00017^{a}	0.00149 ± 0.00007^{a,b}	–
1-Tetradecanol	B	19	0.0104 ± 0.0006^{b}	0.0097 ± 0.0011^{b}	0.0128 ± 0.0014^{c}	0.00526 ± 0.00003^{a}	0.0096 ± 0.0007^{b}
		20	0.0044 ± 0.0004^{a}	0.0054 ± 0.0005^{a,b}	0.0084 ± 0.0015^{c}	0.0053 ± 0.0003^{a,b}	0.0057 ± 0.0009^{b}
		21	0.0088 ± 0.0010^{a}	0.0078 ± 0.0003^{a}	0.0089 ± 0.0007^{a}	0.0090 ± 0.0010^{a}	0.00895 ± 0.00022^{a}
1-Heptadecanol	C	19	0.00132 ± 0.00007^{b}	0.0017 ± 0.0003^{c}	0.00092 ± 0.00011^{a}	0.00128 ± 0.00005^{a,b}	0.00136 ± 0.00015^{b,c}
		20	–	–	0.00129 ± 0.00011	–	–
		21	0.00143 ± 0.00008^{a}	0.0024 ± 0.0003^{b}	0.00131 ± 0.00019^{a}	–	0.0026 ± 0.0003^{b}
Total of alcohols		19	7.64 ± 0.22^{a}	9.0 ± 0.3^{a}	8.1 ± 0.7^{a}	7.74 ± 0.15^{a}	8.7 ± 1.4^{a}
		20	7.10 ± 0.06^{c}	8.3 ± 1.0^{b,c}	10.6 ± 0.5^{a}	8.9 ± 0.6^{b}	8.6 ± 0.5^{b,c}
		21	4.58 ± 0.11^{a}	3.36 ± 0.47^{b}	3.00 ± 0.18^{b}	3.24 ± 0.17^{b}	3.53 ± 0.09^{b}
Aldehydes							
2-Methyl-butanal	B	19	0.00983 ± 0.00005^{c}	0.0110 ± 0.0012^{c}	0.0072 ± 0.0006^{b}	0.0054 ± 0.0005^{a,b}	0.0041 ± 0.0005^{a}
		20	0.046 ± 0.005^{c}	0.038 ± 0.005^{b}	0.0521 ± 0.0005^{d}	0.0258 ± 0.0024^{a}	0.0255 ± 0.0011^{a}
		21	0.0088 ± 0.0010^{b}	0.00558 ± 0.00013^{a}	0.0065 ± 0.0003^{a}	0.0071 ± 0.0010^{a}	0.0107 ± 0.0003^{b}
3-Methyl-1-butanal	B	19	0.009819 ± 0.000015^{c}	0.0112 ± 0.0006^{c}	0.0069 ± 0.0006^{b}	0.0055 ± 0.0008^{b}	0.0037 ± 0.0005^{a}
		20	0.044 ± 0.005^{b}	0.045 ± 0.005^{b}	0.0427 ± 0.0011^{b}	0.027 ± 0.003^{a}	0.0266 ± 0.0009^{a}
		21	0.0090 ± 0.0006^{b}	0.0042 ± 0.0005^{a}	0.0055 ± 0.0003^{a}	0.0057 ± 0.0004^{a}	0.0097 ± 0.0012^{b}
Pentanal	B	19	0.00240 ± 0.00003^{a,b}	0.00201 ± 0.00018^{a}	0.0025 ± 0.0004^{a,b}	0.0028 ± 0.0003^{b}	0.00266 ± 0.00013^{b}
		20	0.00320 ± 0.00019^{a}	0.00706 ± 0.00008^{c}	0.00947 ± 0.00012^{d}	0.00670 ± 0.00011^{b}	0.00666 ± 0.00005^{b}
		21	0.00386 ± 0.00004^{a}	0.00968 ± 0.00018^{d}	0.0074 ± 0.0003^{b,c}	0.00755 ± 0.00006^{c}	0.00712 ± 0.00003^{b}
Hexanal	A	19	0.356 ± 0.018^{c}	0.348 ± 0.012^{c}	0.18 ± 0.03^{b}	0.089 ± 0.004^{a}	0.039 ± 0.018^{a}
		20	0.322 ± 0.014^{c}	0.117 ± 0.005^{a}	0.36 ± 0.04^{c}	0.523 ± 0.011^{d}	0.201 ± 0.010^{b}
		21	0.84 ± 0.05^{a}	1.6 ± 0.3^{b}	1.38 ± 0.19^{b}	1.20 ± 0.16^{a,b}	1.37 ± 0.19^{b}
trans-3-Hexenal	B	19	0.0061 ± 0.0008^{c}	0.0034 ± 0.0005^{a}	0.0057 ± 0.0004^{b,c}	0.004428 ± 0.000009^{a,b}	0.0050 ± 0.0007^{b,c}
		20	0.0048 ± 0.0004^{b}	0.0085 ± 0.0007^{c}	0.0059 ± 0.0003^{b}	0.0083 ± 0.0010^{c}	0.00259 ± 0.00020^{a}
		21	0.00641 ± 0.00007^{a}	0.00595 ± 0.00077^{a}	0.01788 ± 0.00234^{c}	0.01431 ± 0.00022^{b}	0.01679 ± 0.00062^{b,c}
cis-3-Hexenal	B	19	0.00228 ± 0.00023^{b}	0.0022 ± 0.0004^{b}	0.001359 ± 0.000005^{a}	0.00243 ± 0.00013^{b}	0.00144 ± 0.00020^{a}
		20	0.00160 ± 0.00024^{a}	0.00182 ± 0.00011^{b}	0.00158 ± 0.00009^{a}	–	–
		21	0.00178 ± 0.00020^{a}	0.0032 ± 0.0005^{a,b}	0.0085 ± 0.0010^{d}	0.0045 ± 0.0005^{b,c}	0.00587 ± 0.00021^{c}
Heptanal	A	19	–	–	–	–	–
		20	–	–	–	–	–
		21	–	–	–	0.00166 ± 0.00007^{b}	0.00014 ± 0.00019^{a}
trans-2-Hexenal	B	19	0.0099 ± 0.0013^{a,b,c}	0.0102 ± 0.0015^{b,c}	0.0116 ± 0.0016^{c}	0.00624 ± 0.00022^{a}	0.0068 ± 0.0010^{a,b}
		20	0.01067 ± 0.00016^{c}	0.013 ± 0.003^{d}	0.01369 ± 0.00009^{d}	0.0087 ± 0.0013^{b}	0.0069 ± 0.0006^{a}
		21	0.0164 ± 0.0008^{a}	0.0169 ± 0.0010^{a,b}	0.038 ± 0.004^{c}	0.0239 ± 0.0016^{b}	0.033 ± 0.005^{c}
cis-2-Hexenal	B	19	0.37 ± 0.07^{a}	0.415 ± 0.007^{a}	0.38 ± 0.05^{a}	0.30 ± 0.04^{a}	0.27 ± 0.04^{a}
		20	0.2842 ± 0.0012^{a}	0.32 ± 0.05^{a}	0.375 ± 0.021^{a}	0.305 ± 0.017^{a}	0.192 ± 0.005^{a}
		21	0.602 ± 0.003^{a,b}	0.60 ± 0.04^{a,b}	1.06 ± 0.16^{c}	0.53 ± 0.08^{a}	0.81 ± 0.12^{b}
Octanal	A	19	–	0.0024 ± 0.0003^{b}	0.00075 ± 0.00010^{a}	0.000921 ± 0.000016^{a}	0.00085 ± 0.00010^{a}
		20	–	–	0.00116 ± 0.00016^{a}	0.00145 ± 0.00014^{b}	–
		21	0.001396 ± 0.000021^{a}	0.00124 ± 0.00014^{a}	0.0027 ± 0.0004^{b}	0.00330 ± 0.00015^{c}	0.00122 ± 0.00009^{a}
2-Heptenal	A	19	0.00088 ± 0.00003^{a}	0.0056 ± 0.0008^{b}	0.00103 ± 0.00005^{a}	0.00196 ± 0.00021^{a}	0.0045 ± 0.0007^{b}

(*continued on next page*)

Table 1 (*continued*)

		Relative peak area* ± SD†					
Volatile Compounds	ID	Harvest	SC	SELL	SELZ	SEZZ	SE4Z
		20	0.00134 ± 0.00007^{a}	0.0045 ± 0.0006^{c}	0.0030 ± 0.0004^{b}	0.00406 ± 0.00021^{c}	0.0026 ± 0.0003^{b}
		21	0.00393 ± 0.00020^{a}	0.0078 ± 0.0012^{b}	0.0082 ± 0.0009^{b}	0.0066 ± 0.0009^{b}	0.0045 ± 0.0004^{a}
Nonanal	B	19	0.0023 ± 0.0003^{a}	0.0044 ± 0.0005^{b}	0.0019 ± 0.0003^{a}	0.00217 ± 0.00005^{a}	0.0024 ± 0.0003^{a}
		20	0.00126 ± 0.00011^{a}	0.00389 ± 0.00019^{d}	0.00345 ± 0.00004^{c}	0.0035 ± 0.0004^{c}	0.00247 ± 0.00003^{b}
		21	0.00615 ± 0.00022^{a}	0.0068 ± 0.0007^{a}	0.0129 ± 0.0018^{b}	0.0119 ± 0.0014^{b}	0.0081 ± 0.0010^{a}
2,4-Hexadienal isomers sum		19	0.0052 ± 0.0004^{c}	0.0045 ± 0.0007^{c}	0.0043 ± 0.0007^{b,c}	0.00218 ± 0.00011^{a}	0.00277 ± 0.00010^{a,b}
		20	0.0202 ± 0.0022^{d}	0.014 ± 0.003^{b}	0.01261 ± 0.00012^{b}	0.0170 ± 0.0014^{c}	0.0060 ± 0.0008^{a}
		21	0.0052 ± 0.0005^{a}	0.0048 ± 0.0003^{a}	0.0112 ± 0.0013^{c}	0.00729 ± 0.00007^{b}	0.0101 ± 0.0009^{c}
3-Furfuraldehyde	C	19	0.00293 ± 0.00014^{b}	0.0050 ± 0.0005^{d}	0.00213 ± 0.00016^{a}	0.00367 ± 0.00008^{c}	0.00315 ± 0.00004^{b,c}
		20	0.00160 ± 0.00008^{a}	0.00253 ± 0.00015^{c}	0.00209 ± 0.00024^{b}	0.00249 ± 0.00010^{c}	0.00198 ± 0.00013^{b}
		21	0.00355 ± 0.00015^{c}	0.0033 ± 0.0003^{c}	0.0028 ± 0.0003^{b}	0.00166 ± 0.00004^{a}	0.001730 ± 0.000005^{a}
trans-2-Octenal	A	19	–	0.00177 ± 0.00018	–	–	–
		20	–	–	0.0021 ± 0.0003^{b}	0.00293 ± 0.00018^{c}	0.00159 ± 0.00006^{a}
		21	–	–	0.0031 ± 0.0004^{b}	0.00235 ± 0.00022^{a}	–
2-Furfuraldehyde	A	19	0.071 ± 0.005^{c}	0.1161 ± 0.0008^{d}	0.0337 ± 0.0019^{a}	0.0585 ± 0.0013^{b}	0.055 ± 0.003^{b}
		20	0.0425 ± 0.0020^{a}	0.098 ± 0.020^{c}	0.074 ± 0.003^{b}	0.064 ± 0.009^{b}	0.034 ± 0.006^{a}
		21	0.099 ± 0.008^{c}	0.043 ± 0.006^{b}	0.043 ± 0.006^{b}	0.0244 ± 0.0008^{a}	0.0342 ± 0.0006^{a,b}
trans,cis-2,4-Heptadienal	B	19	0.00192 ± 0.00017^{a,b}	0.0028 ± 0.0003^{b}	0.00162 ± 0.00010^{a}	0.00227 ± 0.00010^{a,b}	0.0022 ± 0.0003^{a,b}
		20	0.00160 ± 0.00011^{a}	0.0043 ± 0.0003^{b}	0.0049 ± 0.0003^{c}	0.00443 ± 0.00021^{b}	0.00444 ± 0.00003^{b}
		21	0.0029 ± 0.0004^{a,b}	0.0038 ± 0.0006^{b,c}	0.0043 ± 0.0005^{c}	0.00339 ± 0.00014^{a,b,c}	0.00278 ± 0.00014^{a}
trans,trans-2,4-Heptadienal	B	19	0.0037 ± 0.0003^{a,b}	0.0029 ± 0.0005^{b}	0.00136 ± 0.00020^{a}	0.0020 ± 0.0003^{a,b}	0.0023 ± 0.0005^{a,b}
		20	0.00322 ± 0.00020^{a}	0.00466 ± 0.00007^{b}	0.0055 ± 0.0003^{c}	0.0068 ± 0.0009^{d}	0.00428 ± 0.00023^{b}
		21	0.00349 ± 0.00026^{a}	0.00435 ± 0.0003^{a,b}	0.00449 ± 0.00053^{a,b}	0.006206 ± 0.00087^{b,c}	0.00516 ± 0.0006^{c}
Decanal	A	19	–	0.00236 ± 0.00003^{b}	–	0.00106 ± 0.00014^{a}	–
		20	–	–	–	–	–
		21	0.00292 ± 0.00037^{a}	0.00421 ± 0.0006^{a}	0.0034 ± 0.00029^{a}	0.00956 ± 0.00128^{b}	0.00436 ± 0.00055^{a}
Benzaldehyde	A	19	0.01035 ± 0.00005^{a}	0.024 ± 0.003^{b}	0.0107 ± 0.0010^{a}	0.0084 ± 0.0004^{a}	0.0096 ± 0.0013^{a}
		20	0.0165 ± 0.0025^{a}	0.0158 ± 0.0014^{a}	0.0140 ± 0.0019^{a}	0.0155 ± 0.0020^{a}	0.038 ± 0.002^{b}
		21	0.0151 ± 0.0017^{b}	0.00984 ± 0.00017^{a}	0.0090 ± 0.0003^{a}	0.00997 ± 0.00003^{a}	0.0102 ± 0.0005^{a}
trans-2-Nonenal	B	19	–	0.001053 ± 0.000024	–	–	–
		20	–	0.00143 ± 0.00005^{b}	–	0.00174 ± 0.00021^{c}	0.00124 ± 0.00015^{a}
		21	0.00134 ± 0.00003^{c}	0.00153 ± 0.00007^{a}	0.00237 ± 0.00013^{c}	0.0020 ± 0.0003^{b}	0.00121 ± 0.00011^{d}
5-Methyl-2-furfuraldehyde	A	19	0.00749 ± 0.00011^{d}	0.0090 ± 0.0007^{e}	0.003795 ± 0.000017^{a}	0.00510 ± 0.00024^{b}	0.0061 ± 0.0004^{c}
		20	0.00606 ± 0.00017^{a}	0.0135 ± 0.0020^{b}	0.0140 ± 0.0024^{b}	0.019 ± 0.003^{b}	0.004560 ± 0.00016^{a}
		21	0.00174 ± 0.0003^{c}	0.00655 ± 0.00007^{b}	0.0067 ± 0.0009^{b}	0.0030 ± 0.0004^{a}	0.00317 ± 0.00014^{a}
cis-2-Decenal	A	19	–	0.00237 ± 0.00014^{b}	–	0.00115 ± 0.00013^{a}	0.000936 ± 0.000022^{a}
		20	–	–	–	–	–
		21	0.0017 ± 0.0003^{a}	0.00133 ± 0.00003^{a}	0.0056 ± 0.0008^{b}	0.00641 ± 0.00018^{b}	0.00205 ± 0.00020^{a}
trans,trans-2,4-Nonadienal	B	19	0.00076 ± 0.00006^{a}	0.00191 ± 0.00010^{b}	–	–	0.00085 ± 0.00003^{a}
		20	0.0026 ± 0.0004^{c}	0.0021 ± 0.0003^{b}	0.00128 ± 0.00011^{a}	0.008137 ± 0.000003^{d}	0.001967 ± 0.000003^{b}
		21	–	–	0.0054 ± 0.0008^{b}	0.0039 ± 0.0006^{a}	–
2-Undecanal	B	19	0.00101 ± 0.00008^{a}	0.00354 ± 0.00008^{c}	0.00104 ± 0.00003^{a}	0.00133 ± 0.00003^{b}	0.00112 ± 0.00003^{a}
		20	–	–	–	–	–
		21	–	–	0.0033 ± 0.0005^{b}	0.0053 ± 0.0008^{c}	0.00144 ± 0.00014^{a}
Safranal	C	19	–	–	–	–	–
		20	0.0035 ± 0.0003^{a}	0.0129 ± 0.0011^{d}	0.0054 ± 0.0008^{b}	0.00698 ± 0.00004^{b,c}	0.0070 ± 0.0011^{c}
		21	–	–	–	–	–
5-Hydroxymethylfurfural	A	19	0.0096 ± 0.0014^{a}	0.027 ± 0.004^{b}	0.0090 ± 0.0017^{a}	0.0091 ± 0.0012^{a}	0.0138 ± 0.0012^{a}
		20	0.0122 ± 0.0010^{a}	0.154 ± 0.023^{c}	0.092 ± 0.019^{b}	0.136 ± 0.020^{c}	0.0140 ± 0.0004^{a}
		21	0.075 ± 0.010^{b}	0.0102 ± 0.0015^{a}	0.0129 ± 0.0019^{a}	0.0044 ± 0.0004^{a}	0.0062 ± 0.0008^{a}
Total of aldehydes		19	0.88 ± 0.08^{a}	1.019 ± 0.014^{a}	0.66 ± 0.09^{b}	0.51 ± 0.08^{b,c}	0.44 ± 0.08^{c}
		20	0.83 ± 0.03^{b,c}	0.9 ± 0.3^{b,c}	1.09 ± 0.05^{a,b}	1.20 ± 0.04^{a}	0.585 ± 0.014^{c}
		21	1.73 ± 0.05^{c}	2.3 ± 0.3^{a,b}	2.7 ± 0.4^{a}	1.9 ± 0.7^{b,c}	2.36 ± 0.10^{a,b}
Ethyl Esters							
Ethyl isovalerate	A	19	0.000921 ± 0.000013^{a}	0.00087 ± 0.00004^{a}	–	–	0.00090 ± 0.00009^{a}

(*continued on next page*)

Table 1 (*continued*)

Volatile Compounds	ID	Relative peak area* ± SD†					
		Harvest	**SC**	**SELL**	**SELZ**	**SEZZ**	**SE4Z**
		20	–	–	–	–	–
		21	0.001239 ± 0.000015^{b}	–	–	–	–
Ethyl hexanoate	A	19	0.0007 ± 0.0001^{a}	0.00133 ± 0.00019^{a,b}	0.00080 ± 0.00005^{a}	0.00101 ± 0.00006^{a}	0.0021 ± 0.0003^{b}
		20	0.00139 ± 0.00011^{a}	0.0028 ± 0.0003^{c}	–	0.0022 ± 0.0003^{b}	0.00355 ± 0.00003^{d}
		21	–	–	–	–	–
Ethyl 4-ethoxybenzoate	B	19	–	–	0.00098 ± 0.00003^{a}	0.00092 ± 0.00005^{a}	0.0017 ± 0.0006^{b}
		20	–	–	–	–	–
		21	0.048 ± 0.007^{b}	–	–	–	0.00129 ± 0.00005^{a}
Total of ethyl esters		19	0.00160 ± 0.00008^{b}	0.00220 ± 0.00014^{b}	0.001772 ± 0.000017^{b}	0.00193 ± 0.00012^{b}	0.0048 ± 0.0012^{a}
		20	0.00139 ± 0.00011^{a}	0.0028 ± 0.0003^{c}	–	0.0022 ± 0.0003^{b}	0.00355 ± 0.00003^{d}
		21	0.049 ± 0.007^{a}	–	–	–	0.00129 ± 0.00005^{b}
Ketones							
Diacetyl	A	19	0.0076 ± 0.0006^{a,b}	0.00961 ± 0.00010^{a,b}	0.0037 ± 0.0005^{a}	0.0085 ± 0.0003^{a,b}	0.0107 ± 0.0011^{b}
		20	0.00558 ± 0.00003^{a,b}	0.0147 ± 0.0016^{d}	0.0086 ± 0.0010^{c}	0.0064 ± 0.0003^{b}	0.0045 ± 0.0006^{a}
		21	0.00446 ± 0.00005^{d}	0.0035 ± 0.0005^{c}	0.00259 ± 0.00020^{b}	0.00175 ± 0.00009^{a}	0.00207 ± 0.00006^{a,b}
4-Methyl-2-pentanone	A	19	0.0292 ± 0.0007^{b}	0.02536 ± 0.00010^{a}	0.0290 ± 0.0015^{b}	0.0269 ± 0.0020^{a,b}	0.0266 ± 0.0008^{a,b}
		20	0.050 ± 0.004^{c}	0.0335 ± 0.0004^{a}	0.0375 ± 0.0019^{b}	0.0314 ± 0.0009^{a}	0.0327 ± 0.0014^{a}
		21	0.03738 ± 0.00020^{b}	0.0407 ± 0.0012^{c}	0.0338 ± 0.0003^{a}	0.0340 ± 0.0021^{a}	0.0368 ± 0.0014^{a,b}
2,3-Pentanedione	A	19	0.00202 ± 0.00015^{b}	0.002692 ± 0.00017^{c}	0.00123 ± 0.00021^{a}	0.002536 ± 0.000004^{b,c}	0.0034 ± 0.0004^{d}
		20	–	0.0063 ± 0.0009^{c}	0.004050 ± 0.000017^{b}	0.0046 ± 0.0007^{b}	0.001430 ± 0.000015^{a}
		21	–	–	–	–	–
4-Methyl-2-hexanone	C	19	0.00176 ± 0.00021^{b,c}	0.0011 ± 0.0016^{b,c}	0.00183 ± 0.00015^{c}	0.001469 ± 0.000023^{a,b}	0.00125 ± 0.00003^{a}
		20	0.00191 ± 0.00008^{b}	0.00147 ± 0.00017^{a}	0.001892 ± 0.000016^{b}	0.00192 ± 0.00007^{b}	0.00183 ± 0.00010^{b}
		21	0.00153 ± 0.00005^{b}	0.0015 ± 0.00006^{a}	0.00155 ± 0.00002^{a}	0.02671 ± 0.00404^{b}	0.04656 ± 0.00213^{c}
2,6-Dimethyl-4-heptanone	A	19	0.00441 ± 0.00006^{a}	0.0064 ± 0.0003^{b,c}	0.0065 ± 0.0003^{c}	0.0053 ± 0.0005^{a,b}	0.0060 ± 0.0006^{b,c}
		20	0.00547 ± 0.00023^{a}	0.0058 ± 0.0005^{a}	0.0071 ± 0.0005^{b}	0.0093 ± 0.0009^{c}	0.0072 ± 0.0012^{b}
		21	0.0073 ± 0.00108^{a}	0.0103 ± 0.00111^{b}	0.00601 ± 0.00002^{a}	0.00756 ± 0.00015^{a}	0.0067 ± 0.00084^{a}
Acetoin	A	19	0.053 ± 0.008^{a}	0.045 ± 0.007^{a}	0.024 ± 0.004^{a}	0.026 ± 0.004^{a}	0.18 ± 0.03^{b}
		20	0.028 ± 0.004^{a}	0.124 ± 0.003^{d}	0.059 ± 0.009^{b}	0.104 ± 0.014^{c}	0.106 ± 0.010^{c}
		21	0.07023 ± 0.0104^{d}	0.02102 ± 0.00269^{a,b}	0.01233 ± 0.00002^{a}	0.02671 ± 0.00404^{b}	0.04656 ± 0.00213^{c}
1-Hydroxy-2-propanone	A	19	0.053 ± 0.007^{b}	0.085 ± 0.004^{d}	0.0304 ± 0.0006^{a}	0.0641 ± 0.0005^{c}	0.066 ± 0.003^{c}
		20	0.0119 ± 0.0004^{a}	0.060 ± 0.003^{e}	0.042 ± 0.003^{d}	0.0346 ± 0.0005^{c}	0.022 ± 0.003^{b}
		21	0.04263 ± 0.00636^{b}	0.01101 ± 0.00159^{a}	0.00917 ± 0.00128^{a}	0.00548 ± 0.00081^{a}	0.01197 ± 0.00158^{a}
2,3-Octanedione	C	19	0.00090 ± 0.00004^{a}	0.00100 ± 0.00008^{a}	0.00111 ± 0.00017^{a}	0.00099 ± 0.00015^{a}	0.00098 ± 0.00018^{a}
		20	0.00124 ± 0.00018^{a}	0.00240 ± 0.00018^{b}	0.00142 ± 0.00013^{a}	0.00223 ± 0.00004^{b}	0.00226 ± 0.00016^{b}
		21	–	–	–	0.00186 ± 0.00028^{a}	0.00166 ± 0.00003^{a}
6-Methyl-5-hepten-2-one	A	19	0.0033 ± 0.0004^{b}	0.0074 ± 0.0007^{d}	0.00248 ± 0.00008^{b}	0.005239 ± 0.000005^{c}	0.00403 ± 0.00011^{b}
		20	0.0070 ± 0.0005^{c}	0.0085 ± 0.0010^{d}	0.00605 ± 0.00021^{b}	0.0046 ± 0.0007^{a}	0.0054 ± 0.0005^{a,b}
		21	0.00436 ± 0.00039^{a}	0.00793 ± 0.00099^{b}	0.00497 ± 0.00066^{a}	0.00725 ± 0.00004^{b}	0.00671 ± 0.00001^{b}
2-Cyclopenten-1-one	A	19	0.00984 ± 0.00014^{b}	0.0141 ± 0.0012^{c}	0.0063 ± 0.0003^{a}	0.0115 ± 0.0005^{b}	0.0107 ± 0.0008^{b}
		20	–	–	–	–	–
		21	0.01015 ± 0.00152^{c}	0.00949 ± 0.00058^{b,c}	0.00788 ± 0.00069^{b}	0.00483 ± 0.00025^{a}	0.00496 ± 0.00015^{a}
1-Hydroxy-2-butanone	A	19	0.0261 ± 0.0015^{b}	0.0354 ± 0.0010^{c}	0.020 ± 0.003^{a}	0.02772 ± 0.00019^{b}	0.0240 ± 0.0010^{b}
		20	0.0066 ± 0.0004^{a}	0.0162 ± 0.0015^{d}	0.0184 ± 0.0006^{e}	0.0138 ± 0.0005^{c}	0.0118 ± 0.0016^{b}
		21	0.01416 ± 0.0021^{b}	0.00646 ± 0.00073^{a}	0.00592 ± 0.00082^{a}	0.00579 ± 0.00073^{a}	0.00761 ± 0.00023^{a}
2-Decanone	A	19	0.001091 ± 0.000004^{a}	0.0021 ± 0.0003^{b}	0.00092 ± 0.00006^{a}	–	0.000893 ± 0.000022^{a}
		20	–	–	–	–	–
		21	0.00225 ± 0.00025^{c}	0.0018 ± 0.00007^{b}	0.00136 ± 0.00003^{a}	0.00167 ± 0.00018^{a,b}	0.00144 ± 0.00001^{a,b}
2-Acetylfuran	A	19	0.00929 ± 0.00003^{b}	0.0144 ± 0.0003^{d}	0.007491 ± 0.000007^{a}	0.0143 ± 0.0008^{d}	0.0126 ± 0.0007^{c}
		20	0.0050 ± 0.0003^{a}	0.0107 ± 0.0013^{c}	0.00764 ± 0.00018^{b}	0.00800 ± 0.00016^{b}	0.0045 ± 0.0007^{a}
		21	0.00939 ± 0.00007^{d}	0.00562 ± 0.00008^{c}	0.0043 ± 0.00062^{b}	0.00324 ± 0.00017^{a}	0.00356 ± 0.00004^{a}

(*continued on next page*)

Table 1 (*continued*)

Volatile Compounds	ID	Relative peak area* ± SD†					
		Harvest	SC	SELL	SELZ	SEZZ	SE4Z
3-Methyl-2-cyclopenten-1-one	C	19	0.00221 ± 0.00005^{b}	0.00279 ± 0.00011^{d}	0.00135 ± 0.00008^{a}	0.00010 ± 0.00018^{c}	0.00244 ± 0.00005^{c}
		20	0.00127 ± 0.00004^{a}	0.0023 ± 0.0003^{c}	0.00188 ± 0.00018^{b}	0.00206 ± 0.00005^{b}	0.00187 ± 0.00021^{b}
		21	0.00249 ± 0.00026^{b}	0.00202 ± 0.00019^{a}	0.0017 ± 0.00008^{a}	–	–
2-Cyclopentene-1,4-dione	B	19	0.0036 ± 0.0003^{b}	0.0058 ± 0.0007^{c}	0.00234 ± 0.00008^{a}	0.00363 ± 0.00012^{b}	0.0060 ± 0.0004^{c}
		20	0.0029 ± 0.0004^{a}	0.0234 ± 0.0012^{c}	0.0121 ± 0.0005^{b}	0.0139 ± 0.0021^{b}	0.00266 ± 0.00013^{a}
		21	0.0159 ± 0.00237^{b}	0.00391 ± 0.00058^{a}	0.00332 ± 0.00049^{a}	0.00191 ± 0.00004^{a}	0.0015 ± 0.00016^{a}
2-Acetyl-5-methylfuran	A	19	0.00096 ± 0.00011^{a}	0.0024 ± 0.0003^{c}	0.00135 ± 0.00005^{b}	0.001685 ± 0.000003^{b}	0.00135 ± 0.00006^{b}
		20	–	–	0.00122 ± 0.00004^{a}	0.0021 ± 0.0003^{b}	–
		21	–	–	–	0.00124 ± 0.00004^{a}	0.0015 ± 0.00016^{a}
2-Undecanone	A	19	–	0.00105 ± 0.00004^{b}	0.000786 ± 0.000010^{a}	–	–
		20	–	–	–	–	–
		21	–	–	–	–	–
Acetophenone	A	19	0.0074 ± 0.0005^{a}	0.0165 ± 0.0024^{b}	0.00689 ± 0.00009^{a}	0.0060 ± 0.0007^{a}	0.0064 ± 0.0009^{a}
		20	0.00704 ± 0.00003^{c}	0.00507 ± 0.00005^{b}	0.0052 ± 0.0006^{b}	0.0073 ± 0.0009^{c}	0.0039 ± 0.0007^{a}
		21	0.10421 ± 0.01549^{c}	0.05915 ± 0.00894^{b}	0.01058 ± 0.00158^{a}	0.01256 ± 0.00027^{a}	0.00832 ± 0.0008^{a}
2-Hydroxy-2-cyclopenten-1-one	C	19	0.0096 ± 0.0003^{a}	0.037 ± 0.005^{c}	0.0175 ± 0.0021^{b}	0.0397 ± 0.0020^{c}	0.0417 ± 0.0015^{c}
		20	–	0.0033 ± 0.0003^{a}	0.00609 ± 0.00016^{b}	0.0038 ± 0.0006^{a}	0.0031 ± 0.0004^{a}
		21	–	–	–	–	–
4-Methyl-5H-furan-2-one	B	19	0.00366 ± 0.00022^{b}	0.0039 ± 0.0003^{b}	0.00280 ± 0.00004^{a}	0.0043 ± 0.0002^{b}	0.0039 ± 0.0005^{b}
		20	0.00184 ± 0.00010^{a}	0.0044 ± 0.0004^{c}	0.00328 ± 0.00019^{b}	0.00332 ± 0.00007^{b}	0.0020 ± 0.0003^{a}
		21	0.0024 ± 0.00036^{a,b}	0.0029 ± 0.00038^{b}	0.00273 ± 0.0002^{a,b}	0.0021 ± 0.0003^{a}	0.00209 ± 0.00003^{a}
Benzophenone	C	19	0.00261 ± 0.00014^{b}	0.0033 ± 0.0007^{b}	0.002617 ± 0.000011^{b}	0.001718 ± 0.000021^{a}	0.00297 ± 0.00017^{b}
		20	0.00238 ± 0.00011^{a}	0.0026 ± 0.0003^{a,b}	0.0044 ± 0.0004^{d}	0.0029 ± 0.0003^{b,c}	0.0032 ± 0.0003^{c}
		21	0.00304 ± 0.00006^{b,c}	0.00327 ± 0.00048^{c}	0.00249 ± 0.00016^{a,b}	0.00216 ± 0.00016^{a}	0.00349 ± 0.00033^{c}
Total of ketones		19	0.23 ± 0.06^{c,d}	0.33 ± 0.03^{a,b}	0.171 ± 0.003^{d}	0.252 ± 0.012^{b,c}	0.41 ± 0.03^{a}
		20	0.13738 ± 0.00010^{d}	0.3217 ± 0.0010^{a}	0.228 ± 0.011^{c}	0.256 ± 0.018^{b}	0.2160 ± 0.0004^{c}
		21	0.33189 ± 0.00505^{a}	0.19194 ± 0.00964^{b}	0.1107 ± 0.00355^{d}	0.12197 ± 0.00687^{d}	0.14953 ± 0.00067^{c}
Lactones							
γ-Butyrolactone	A	19	0.032 ± 0.005^{b,c}	0.0410 ± 0.0017^{c}	0.0142 ± 0.0008^{a}	0.0310 ± 0.0008^{b}	0.030 ± 0.003^{b}
		20	0.0089 ± 0.0004^{a}	0.0164 ± 0.0011^{c,d}	0.0100 ± 0.0014^{a,b}	0.0136 ± 0.0013^{b,c}	0.020 ± 0.003^{d}
		21	0.0141 ± 0.0004^{c}	0.0084 ± 0.0011^{a}	0.007573 ± 0.000014^{a}	0.00852 ± 0.00008^{a,b}	0.0102 ± 0.0009^{b}
2,5-Dihydro-3,2-furanone	C	19	0.00099 ± 0.00004^{b}	–	0.000775 ± 0.000010^{a}	0.00102 ± 0.00005^{b}	0.00079 ± 0.00011^{a}
		20	–	0.00153 ± 0.00020	–	–	–
		21	–	–	–	–	–
2(5H)-Furanone	B	19	0.025 ± 0.003^{a}	0.0490 ± 0.0019^{c}	0.0238 ± 0.0023^{a}	0.0398 ± 0.0016^{b}	0.041 ± 0.003^{b}
		20	0.00726 ± 0.00020^{a}	0.033 ± 0.003^{d}	0.02173 ± 0.00023^{c}	0.020 ± 0.003^{c}	0.0112 ± 0.0020^{b}
		21	0.021 ± 0.003^{b}	0.0112 ± 0.0015^{a}	0.0077 ± 0.0008^{a}	0.0109 ± 0.0014^{a}	0.0108 ± 0.0010^{a}
Cyclotene	A	19	0.0144 ± 0.0018^{b}	0.0174 ± 0.0009^{c}	0.0096 ± 0.0006^{a}	0.01785 ± 0.00016^{c}	0.0185 ± 0.0004^{c}
		20	0.0022 ± 0.0008^{a,b}	0.0142 ± 0.0006^{b}	0.00805 ± 0.00010^{a,b}	0.0088 ± 0.0010^{a,b}	0.0051 ± 0.0003^{a}
		21	0.0147 ± 0.0022^{c}	0.0052 ± 0.0008^{b}	0.00433 ± 0.00004^{a,b}	0.00210 ± 0.00008^{a}	0.00165 ± 0.00016^{a}
γ-Nonalactone	A	19	0.0105 ± 0.0017^{b}	0.0102 ± 0.0005^{b}	0.0076 ± 0.0003^{a}	0.0102 ± 0.0007^{b}	0.0087 ± 0.0009^{a,b}
		20	0.00615 ± 0.00006^{a}	0.0165 ± 0.0006^{c}	0.0114 ± 0.0008^{b}	0.0100 ± 0.0011^{b}	0.018 ± 0.003^{c}
		21	0.00729 ± 0.00020^{c}	0.00476 ± 0.00006^{a,b}	0.0042 ± 0.0003^{a}	0.0039 ± 0.0003^{a}	0.0054 ± 0.0007^{b}
γ-Decalactone	A	19	0.002248 ± 0.000019^{a}	0.0036 ± 0.0004^{b}	0.00185 ± 0.00014^{a}	0.00212 ± 0.00007^{a}	0.00213 ± 0.00021^{a}
		20	0.00190 ± 0.00018^{a}	0.00226 ± 0.00020^{b,c}	0.002390 ± 0.000021^{c}	0.0026 ± 0.0002^{d}	0.00215 ± 0.00005^{b}
		21	0.00198 ± 0.00018^{a}	0.00275 ± 0.00007^{a}	0.00215 ± 0.00022^{a}	0.00182 ± 0.00005^{b}	0.0033 ± 0.0004^{b}
Dihydroactinidiolide	C	19	0.0040 ± 0.0006^{b}	0.0030 ± 0.0003^{a}	0.0026 ± 0.0003^{a}	0.0044 ± 0.0007^{b}	0.0061 ± 0.0009^{b}
		20	0.0029 ± 0.0006^{a}	0.0066 ± 0.0015^{c}	0.0042 ± 0.0005^{b}	0.0047 ± 0.0007^{b}	0.00607 ± 0.00018^{c}
		21	0.0034 ± 0.0004^{c}	0.0032 ± 0.0004^{c}	0.002156 ± 0.000013^{a}	0.00247 ± 0.00006^{a,b}	0.00295 ± 0.00022^{b,c}
Total of lactones		19	0.089 ± 0.010^{c}	0.1243 ± 0.0011^{a}	0.0604 ± 0.0010^{d}	0.1064 ± 0.0006^{b}	0.107 ± 0.008^{b}
		20	0.036 ± 0.008^{c}	0.091 ± 0.006^{a}	0.0578 ± 0.0008^{b}	0.060 ± 0.006^{b}	0.062 ± 0.008^{b}
		21	0.062 ± 0.005^{a}	0.0355 ± 0.0024^{b}	0.0281 ± 0.0010^{c}	0.0297 ± 0.0015^{b,c}	0.0345 ± 0.0011^{b,c}
Methyl Esters							
Methyl octanoate	B	19	–	–	–	–	–
		20	–	–	–	–	–

(*continued on next page*)

Table 1 (*continued*)

Volatile Compounds	ID	Harvest	Relative peak area* ± SD† SC	SELL	SELZ	SEZZ	SE4Z
		21	–	–	–	–	0.01195 ± 0.00178
Methyl pyruvate	C	19	0.0071 ± 0.0005[a]	0.013 ± 0.003[b]	–	0.0210 ± 0.0009[c]	–
		20	0.0046 ± 0.0003[a]	0.074 ± 0.009[c]	0.0229 ± 0.0013[b]	0.023 ± 0.003[b]	0.0123 ± 0.0009[a,b]
		21	–	–	–	–	0.00169 ± 0.00025
Methyl nonanoate	A	19	–	–	0.0017 ± 0.0003	–	–
		20	–	–	–	–	–
		21	–	–	–	–	0.00251 ± 0.00025
Methyl decanoate	A	19	–	–	0.00139 ± 0.00021[a]	–	0.00074 ± 0.00006[b]
		20	–	–	–	–	–
		21	–	–	–	–	0.0081 ± 0.0007
Methyl salicylate	A	19	0.0056 ± 0.0007[c]	0.00167 ± 0.00014[a]	0.00117 ± 0.00012[a]	0.0029 ± 0.0003[b]	0.00142 ± 0.00013[a]
		20	0.00176 ± 0.00022[a]	0.00316 ± 0.00006[b]	0.00165 ± 0.00022[a]	0.00178 ± 0.00019[a]	–
		21	0.00184 ± 0.00022[b]	0.001268 ± 0.000024[a]	0.00119 ± 0.00010[a]	–	–
Methyl hexadecanoate	A	19	0.0053 ± 0.0008[a,b]	0.0056 ± 0.0008[a,b]	0.0174 ± 0.0015[c]	0.00260 ± 0.00024[a]	0.0068 ± 0.0010[b]
		20	0.0046 ± 0.0008[a]	0.00397 ± 0.00009[a]	0.022 ± 0.003[b]	0.0028 ± 0.0005[a]	0.0029 ± 0.0004[a]
		21	0.00425 ± 0.00010[a]	0.00330 ± 0.00020[a]	0.0087 ± 0.0013[b]	0.0055 ± 0.0008[a,b]	0.0218 ± 0.0023[c]
Methyl dihydrojasmonate	A	19	0.0107 ± 0.0012[a,b]	0.0264 ± 0.0008[c]	0.0129 ± 0.0011[b]	0.01028 ± 0.00015[a]	0.0100 ± 0.0006[a]
		20	0.0056 ± 0.0003[b]	0.0040 ± 0.0004[a]	0.0106 ± 0.0015[d]	0.0093 ± 0.0009[c]	0.0059 ± 0.0006[b]
		21	0.0156 ± 0.0021[b]	0.0081 ± 0.0006[a]	0.00844 ± 0.00025[a]	0.0061 ± 0.0008[a]	0.0083 ± 0.0006[a]
Total of methyl esters		19	0.029 ± 0.004[c]	0.0462 ± 0.0004[a]	0.0346 ± 0.0015[b]	0.0368 ± 0.0007[b]	0.0190 ± 0.0018[d]
		20	0.0165 ± 0.0006[d]	0.085 ± 0.009[a]	0.057 ± 0.014[b]	0.037 ± 0.006[c]	0.0211 ± 0.0007[c,d]
		21	0.0217 ± 0.0018[b]	0.0127 ± 0.0007[c,d]	0.0183 ± 0.0016[b,c]	0.0115 ± 0.0016[d]	0.054 ± 0.005[a]
Nitrogen Compounds							
2-Methylpyrazine	A	19	0.00298 ± 0.00004[b]	0.00360 ± 0.00005[c]	0.00135 ± 0.00017[a]	0.00185 ± 0.00005[a]	0.00143 ± 0.00008[a]
		20	0.00115 ± 0.00013[a]	0.00249 ± 0.00009[d]	0.00237 ± 0.00003[d]	0.00175 ± 0.00006[b]	0.0020 ± 0.0003[c]
		21	–	–	–	–	–
Pyrrole	A	19	0.0061 ± 0.0004[b,c]	0.0066 ± 0.0004[c]	0.00459 ± 0.00017[a]	0.0051 ± 0.0005[a,b]	0.0047 ± 0.0005[a]
		20	0.00266 ± 0.00009[a]	0.0041 ± 0.0003[c]	0.00348 ± 0.00018[b]	0.00259 ± 0.00021[a]	0.0036 ± 0.0007[b]
		21	0.00312 ± 0.00009[a]	0.0030 ± 0.0004[a]	0.0025 ± 0.0003[a]	0.0041 ± 0.0006[b]	0.00270 ± 0.00005[a]
1-Ethyl-2-pyrrolidone	C	19	–	–	–	0.0025 ± 0.003	–
		20	–	–	–	–	–
		21	–	0.00157 ± 0.00012[a,b]	0.00168 ± 0.00005[b]	0.001495 ± 0.000011[a]	0.00162 ± 0.00010[a,b]
1,2-Benzisothiazole	C	19	0.00372 ± 0.00007[a]	0.0048 ± 0.0007[a]	0.00444 ± 0.00017[a]	0.0049 ± 0.0007[a]	0.0045 ± 0.0004[a]
		20	0.00936 ± 0.00003[a]	0.0120 ± 0.0006[b]	0.0119 ± 0.0012[b]	0.0103 ± 0.0011[a]	0.0102 ± 0.0006[a]
		21	0.0061 ± 0.0003[b,c]	0.0073 ± 0.0010[c]	0.00390 ± 0.00020[a]	0.00457 ± 0.00009[a]	0.005887 ± 0.000017[b]
Total of nitrogen compounds		19	0.0128 ± 0.0004[b]	0.0150 ± 0.0012[a]	0.01038 ± 0.00018[c]	0.0144 ± 0.0009[b,c]	0.0106 ± 0.0003[b,c]
		20	0.013167 ± 0.000010[d]	0.0187 ± 0.0005[a]	0.0178 ± 0.0014[a,b]	0.0146 ± 0.0010[c,d]	0.0158 ± 0.0004[b,c]
		21	0.00924 ± 0.00020[b,c]	0.0118 ± 0.0007[a]	0.0081 ± 0.0006[c]	0.0102 ± 0.0007[b]	0.01020 ± 0.00003[b]
C_{13}-Norisoprenoids							
α-Ionone	C	19	–	0.00098 ± 0.00015[a]	0.00165 ± 0.00021[a,b]	0.0029 ± 0.0004[b,c]	–
		20	–	–	–	–	–
		21	–	–	–	–	–
β-Damascenone	A	19	0.0100 ± 0.0007[a]	0.0119 ± 0.0006[a]	0.0155 ± 0.0018[a,b]	0.022 ± 0.003[b]	0.010 ± 0.003[a]
		20	0.0093 ± 0.0003[b]	0.0113 ± 0.0024[b,c]	0.0123 ± 0.0010[c]	0.0147 ± 0.0022[d]	0.0038 ± 0.0006[a]
		21	0.0093 ± 0.0003[a]	0.0155 ± 0.0023[b,c]	0.018 ± 0.003[c]	0.0146 ± 0.0022[b,c]	0.0106 ± 0.0010[a,b]
β-Ionone	B	19	0.00177 ± 0.00018[b,c]	0.00210 ± 0.00018[c]	0.00166 ± 0.00012[b]	0.00129 ± 0.00008[a]	0.00156 ± 0.00013[a,b]
		20	–	–	–	0.00154 ± 0.00023	–
		21	0.00162 ± 0.00007[a]	0.00159 ± 0.00022[a]	0.00159 ± 0.00023[a]	0.0019 ± 0.0003[a]	0.00170 ± 0.00006[a]
Total of C_{13}-norisoprenoids		19	0.0118 ± 0.0009[b]	0.0150 ± 0.0010[b]	0.0188 ± 0.0015[a,b]	0.027 ± 0.007[a]	0.011 ± 0.003[b]
		20	0.0093 ± 0.0003[b]	0.0113 ± 0.0024[b]	0.0123 ± 0.0010[a,b]	0.0162 ± 0.0017[a]	0.0038 ± 0.0018[c]
		21	0.0109 ± 0.0004[c]	0.0171 ± 0.0021[a,b]	0.0194 ± 0.0024[a]	0.0165 ± 0.0015[a,b]	0.0124 ± 0.0010[b,c]
Other Esters							
Isopropyl laurate	A	19	–	0.00103 ± 0.00005[b,c]	0.00075 ± 0.00008[a]	0.00085 ± 0.00012[a,b]	0.00114 ± 0.00003[c]
		20	–	–	–	–	–
		21	–	–	–	–	–
Isopropyl myristate	A	19	0.00204 ± 0.00009[a]	0.0028 ± 0.0004[b,c]	0.0023 ± 0.0004[a,b]	0.00171 ± 0.00008[a]	0.00340 ± 0.00014[c]
		20	–	–	–	–	–
		21	0.00138 ± 0.00019[a]	–	–	0.00140 ± 0.00009[a]	0.00196 ± 0.00025[b]
Hexyl salicylate	A	19	0.0069 ± 0.0005[a,b]	0.0095 ± 0.0004[c]	0.0082 ± 0.0017[b,c]	0.0046 ± 0.0004[a]	0.0103 ± 0.0010[c]
		20	–	0.00146 ± 0.00011[a]	0.0037 ± 0.0005[c]	0.0025 ± 0.0004[b]	0.0019 ± 0.0002[a]
		21	0.00142 ± 0.00016[a]	0.001551 ± 0.000020[a]	0.00162 ± 0.00015[a]	0.001564 ± 0.000011[a]	0.00429 ± 0.00006[b]
Isopropyl palmitate	A	19			0.0024 ± 0.0003[c]	0.00084 ± 0.00004[a]	0.00203 ± 0.00020[c]

(*continued on next page*)

Table 1 (*continued*)

Volatile Compounds	ID	Relative peak area* ± SD†					
		Harvest	SC	SELL	SELZ	SEZZ	SE4Z
			0.001372 ± 0.000009^{b}	0.00151 ± 0.00016^{b}			
		20	–	–	–	–	–
		21	0.0021 ± 0.0003^{b}	0.00147 ± 0.00022^{a}	–	–	0.0022 ± 0.0003^{b}
Total of other esters		19	0.0099 ± 0.0015^{c}	0.0148 ± 0.0010^{b,c}	0.0136 ± 0.0009^{a,b}	0.0080 ± 0.0006^{d}	0.0169 ± 0.0014^{a}
		20	–	0.00146 ± 0.00011^{a}	0.0037 ± 0.0005^{c}	0.0025 ± 0.0004^{b}	0.0019 ± 0.0002^{a}
		21	0.00494 ± 0.00004^{b}	0.00302 ± 0.00020^{c}	0.00162 ± 0.00015^{d}	0.00297 ± 0.00010^{c}	0.00850 ± 0.00014^{a}
Others							
Dimethyl disulphide	B	19	0.00121 ± 0.00003^{b}	0.00141 ± 0.00004^{c}	0.000743 ± 0.000007^{a}	0.00086 ± 0.00007^{a}	0.00079 ± 0.00007^{a}
		20	0.0029 ± 0.0004^{d}	0.0020 ± 0.0003^{c}	0.00128 ± 0.00015^{a}	0.00165 ± 0.00019^{b}	–
		21	0.00188 ± 0.00006^{b}	0.00177 ± 0.00023^{a,b}	0.00176 ± 0.00023^{a,b}	0.00153 ± 0.00003^{a}	–
3,5,5-Trimethyl-2-hexene	C	19	0.0079 ± 0.0005^{a}	0.0115 ± 0.0010^{a}	0.028 ± 0.004^{b}	0.0205 ± 0.0019^{b}	0.028 ± 0.004^{a,b}
		20	0.0029 ± 0.0004^{a}	0.0087 ± 0.0004^{d}	0.0063 ± 0.0003^{c}	0.005378 ± 0.000024^{b}	0.0055 ± 0.0003^{b}
		21	0.0104 ± 0.0015^{c}	0.00358 ± 0.00008^{a}	0.0035 ± 0.0003^{a}	0.0053 ± 0.0003^{a}	0.0073 ± 0.0004^{b}
Total of others		19	0.0091 ± 0.0005^{b}	0.0129 ± 0.0011^{b}	0.029 ± 0.004^{a}	0.0214 ± 0.0019^{a,b}	0.029 ± 0.012^{a}
		20	0.0058 ± 0.0003^{a}	0.01061 ± 0.0020^{c}	0.00761 ± 0.00012^{b}	0.00703 ± 0.00022^{b}	0.0055 ± 0.0003^{a}
		21	0.0123 ± 0.0015^{a}	0.00535 ± 0.00006^{c}	0.0054 ± 0.0005^{c}	0.0068 ± 0.0003^{b,c}	0.0073 ± 0.0004^{b}
Terpenes							
β-Pinene	B	19	0.00095 ± 0.00014^{a}	0.0030 ± 0.0004^{b}	0.001017 ± 0.000019^{a}	0.00101 ± 0.00012^{a}	0.00079 ± 0.00004^{a}
		20	–	–	–	–	–
		21	–	–	–	–	–
Limoneno	A	19	0.0051 ± 0.0007^{a}	0.050 ± 0.004^{b}	0.0116 ± 0.0013^{a}	0.0066 ± 0.0011^{a}	0.0111 ± 0.0016^{a}
		20	–	–	0.00191 ± 0.00005^{a}	0.0033 ± 0.0005^{a}	0.0029 ± 0.0004^{a}
		21	–	–	–	–	–
p-Cymene	A	19	0.00181 ± 0.00008^{a}	0.0101 ± 0.0014^{c}	0.00241 ± 0.00018^{a,b}	0.0026 ± 0.0004^{a,b}	0.00411 ± 0.00020^{b}
		20	0.00128 ± 0.00014	–	–	–	–
		21	–	–	–	–	–
cis-linalool oxide	A	19	0.00209 ± 0.00016^{a}	0.0031 ± 0.0004^{a,b}	0.00356 ± 0.00010^{a,b}	0.0111 ± 0.0010^{c}	0.0057 ± 0.0009^{b}
		20	0.00140 ± 0.00007^{a}	0.00276 ± 0.00006^{d}	0.00171 ± 0.00019^{b}	0.00204 ± 0.00021^{c}	0.0016 ± 0.0004^{a,b}
		21	0.0017 ± 0.00012	0.00238 ± 0.00008	0.00210 ± 0.00003	0.00179 ± 0.00024	0.0029 ± 0.0004
Dihydromyrcenol + *trans*-linalool oxide	A	19	0.0027 ± 0.0005^{a}	0.0113 ± 0.0014^{b}	0.0094 ± 0.0014^{b}	0.035 ± 0.005^{d}	0.0227 ± 0.012^{c}
		20	–	–	0.0015 ± 0.0003	–	–
		21	0.00330 ± 0.00010^{b}	0.00524 ± 0.00041^{a}	0.00286 ± 0.00021^{b}	0.00207 ± 0.00004^{c}	0.00309 ± 0.00001^{b}
Linalool	A	19	0.00307 ± 0.00009^{b}	0.00420 ± 0.00024^{c}	0.00370 ± 0.00009^{b,c}	0.0038 ± 0.0005^{c}	0.00222 ± 0.00024^{a}
		20	0.001259 ± 0.000021^{a}	0.00185 ± 0.00018^{b}	0.00167 ± 0.00011^{b}	0.00136 ± 0.00017^{a}	0.00139 ± 0.00013^{a}
		21	–	–	0.00124 ± 0.00006^{a}	–	0.00144 ± 0.00021^{a}
Hotrienol	C	19	0.00152 ± 0.00015^{a}	0.0061 ± 0.0009^{c}	0.0028 ± 0.0004^{b}	0.00147 ± 0.00022^{a}	0.00106 ± 0.00006^{a}
		20	–	0.0039 ± 0.0006^{b}	0.00234 ± 0.00016^{a}	–	0.00139 ± 0.00021^{a}
		21	0.00315 ± 0.00033^{b}	0.00235 ± 0.00016^{a}	0.00241 ± 0.00036^{a}	0.00205 ± 0.0001^{a}	0.00224 ± 0.00033^{a}
Menthol	A	19	0.00162 ± 0.00003^{a}	0.0033 ± 0.0003^{c}	0.00189 ± 0.00008^{a,b}	0.00178 ± 0.00007^{a}	0.0024 ± 0.0004^{b}
		20	–	–	–	–	–
		21	0.00153 ± 0.00010^{a}	0.00203 ± 0.00021^{b}	–	0.00148 ± 0.00018^{a}	–
α-Terpineol	A	19	0.000999 ± 0.000014^{a}	0.00139 ± 0.00008^{b}	0.00133 ± 0.00005^{b}	0.00170 ± 0.00016^{c}	0.000965 ± 0.00012^{a}
		20	–	–	–	–	–
		21	–	–	–	–	–
Epoxylinalol	A	19	0.00154 ± 0.00020^{a}	0.0038 ± 0.0005^{a}	0.0060 ± 0.0007^{a}	0.026 ± 0.003^{c}	0.019 ± 0.003^{b}
		20	–	0.0024 ± 0.0003^{a}	0.00249 ± 0.000017^{a}	0.0039 ± 0.0004^{b}	0.0031 ± 0.0004^{a}
		21	0.001329 ± 0.000005^{a}	0.00139 ± 0.00021^{a}	–	–	–
Geranyl acetone	B	19	0.00639 ± 0.00003^{b}	0.0072 ± 0.0009^{b}	0.0061 ± 0.0005^{b}	0.00404 ± 0.00016^{a}	0.0066 ± 0.0007^{b}
		20	0.0049 ± 0.0006^{b}	0.0034 ± 0.0005^{a}	0.0047 ± 0.0007^{c}	0.00613 ± 0.00003^{d}	0.0026 ± 0.0002^{a}
		21	0.00353 ± 0.00025^{a}	0.0033 ± 0.0004^{a}	0.0039 ± 0.0005^{a}	0.01037 ± 0.00024^{c}	0.0077 ± 0.0007^{b}
Nerol	B	19	0.0153 ± 0.0006^{b,c}	0.0203 ± 0.0004^{d}	0.0138 ± 0.0007^{b}	0.01662 ± 0.00017^{c}	0.0089 ± 0.0013^{a}
		20	0.00818 ± 0.00017^{d}	0.0055 ± 0.0006^{b}	0.0061 ± 0.0003^{c}	0.00396 ± 0.00020^{a}	0.0054 ± 0.0003^{b}
		21	0.0070 ± 0.0003^{c}	0.0035 ± 0.0005^{b}	0.00197 ± 0.00015^{a}	0.0021 ± 0.0003^{a}	0.00156 ± 0.00015^{a}
Total of terpenes		19	0.0430 ± 0.0003^{c}	0.124 ± 0.006^{a}	0.0637 ± 0.0019^{c}	0.112 ± 0.006^{a,b}	0.076 ± 0.018^{b}

(*continued on next page*)

Table 1 (*continued*)

Volatile Compounds	ID	Relative peak area* ± SD†					
		Harvest	SC	SELL	SELZ	SEZZ	SE4Z
		20	0.0170 ± 0.0007^{c}	0.0198 ± 0.0015^{a,b}	0.0208 ± 0.0008^{a}	0.0206 ± 0.0005^{a}	0.0184 ± 0.0012^{b,c}
		21	0.02155 ± 0.0004^{a}	0.0204 ± 0.0018^{a}	0.0145 ± 0.0013^{b}	0.01982 ± 0.00013^{a}	0.01895 ± 0.00009^{a}
Volatile Phenols							
Veratrol	A	19	–	–	0.00110 ± 0.00013^{a}	0.00620 ± 0.00003^{a}	0.034 ± 0.005^{b}
		20	–	–	–	–	–
		21	–	–	–	–	–
Guaiacol	A	19	0.0080 ± 0.0010^{b}	0.0089 ± 0.0013^{b,c}	0.0050 ± 0.0003^{a}	0.0063 ± 0.0003^{a,b}	0.0117 ± 0.0013^{c}
		20	0.00242 ± 0.00012^{a,b}	0.00285 ± 0.00006^{b}	0.00243 ± 0.00012^{a,b}	0.00212 ± 0.00010^{a}	0.0028 ± 0.0004^{b}
		21	0.0036 ± 0.0003^{b}	0.00341 ± 0.00010^{b}	0.00167 ± 0.00010^{a}	0.00152 ± 0.00008^{a}	–
o-Cresol	B	19	0.00250 ± 0.00009^{b}	0.00306 ± 0.00003^{c}	0.00162 ± 0.00004^{a}	0.003105 ± 0.000005^{c}	0.0036 ± 0.0005^{c}
		20	0.00138 ± 0.00004^{b,c}	0.00128 ± 0.00003^{a}	0.00137 ± 0.00010^{b}	–	0.00147 ± 0.00007^{c}
		21	0.00164 ± 0.00013	–	–	–	–
3-Phenoxy-1-propanol	B	19	0.0029 ± 0.0003^{a}	0.0042 ± 0.0006^{b}	0.00345 ± 0.00003^{a,b}	0.0032 ± 0.0003^{a,b}	0.0029 ± 0.0003^{a,b}
		20	–	–	–	–	–
		21	–	–	–	–	–
p-Cresol	A	19	0.00344 ± 0.00008^{c}	0.00302 ± 0.00005^{b}	0.00196 ± 0.00003^{a}	0.0023 ± 0.0002^{a}	0.00202 ± 0.00017^{a}
		20	0.0014 ± 0.00021^{a}	0.00172 ± 0.00004^{b}	0.00234 ± 0.00005^{c}	0.00180 ± 0.00005^{b}	0.00176 ± 0.00013^{b}
		21	0.00232 ± 0.0003^{b,c}	0.00206 ± 0.00013^{a,b}	0.00214 ± 0.00010^{a,b}	0.0016 ± 0.0003^{a}	0.0029 ± 0.0003^{c}
5-Pentylresorcinol	C	19	0.0116 ± 0.0007^{b,c}	0.00946 ± 0.00018^{b}	0.0041 ± 0.0004^{a}	0.0044 ± 0.0004^{a}	0.0129 ± 0.0014^{c}
		20	0.0077 ± 0.0011^{a}	0.0280 ± 0.0024^{d}	0.0204 ± 0.0020^{c}	0.0178 ± 0.0019^{b}	0.0179 ± 0.0006^{b}
		21	0.0189 ± 0.0012^{a}	0.027 ± 0.004^{b}	0.025836 ± 0.000016^{b}	0.0252 ± 0.0024^{b}	0.0265 ± 0.0004^{b}
Eugenol	A	19	0.00130 ± 0.00023^{a}	0.00135 ± 0.00005^{a}	0.00126 ± 0.00004^{a}	0.0023 ± 0.0003^{a,b}	0.0049 ± 0.0018^{b}
		20	–	–	–	–	–
		21	–	–	–	–	–
4-Ethylphenol	A	19	0.00079 ± 0.00003	–	–	–	–
		20	–	–	–	–	–
		21	–	–	0.00136 ± 0.00014	–	–
4-Vinylguaiacol	A	19	0.00085 ± 0.00004^{a}	–	0.001181 ± 0.000013^{b}	0.00286 ± 0.00012^{c}	0.001153 ± 0.000020^{b}
		20	–	–	–	–	–
		21	0.0036 ± 0.0004^{d}	0.0024 ± 0.0003^{b,c}	0.00128 ± 0.00015^{a}	0.0020 ± 0.0003^{a,b}	0.002723 ± 0.000018^{c}
2-Ethylhexyl 4-methylbenzoate	C	19	–	–	–	–	–
		20	0.00302 ± 0.00008^{a}	0.0030 ± 0.0003^{a}	0.0035 ± 0.0004^{a,b}	0.0042 ± 0.0006^{b}	0.0033 ± 0.0003^{a,b}
		21	0.0079 ± 0.0012^{a}	0.01245 ± 0.0010^{c}	0.0109 ± 0.0008^{b,c}	0.0060 ± 0.0009^{a}	0.0084 ± 0.0012^{a,b}
α-Hexylcinnamaldehyde	C	19	0.00177 ± 0.000003^{b}	0.0019 ± 0.0003^{b}	0.0025 ± 0.0003^{c}	0.00098 ± 0.00006^{a}	0.00294 ± 0.00016^{c}
		20	–	–	–	–	–
		21	–	–	–	–	0.00157 ± 0.00012
Coumaran	C	19	0.0122 ± 0.0009^{a}	0.01140 ± 0.00023^{a}	0.0152 ± 0.0017^{a}	0.032 ± 0.004^{b}	0.0129 ± 0.0004^{a}
		20	0.0036 ± 0.0006^{a}	0.0057 ± 0.0003^{c}	0.00423 ± 0.00009^{b}	0.0055 ± 0.0004^{c}	0.0046 ± 0.0003^{b}
		21	0.0141 ± 0.0009^{b}	0.0099 ± 0.0009^{a}	0.0083 ± 0.0005^{a}	0.0090 ± 0.0013^{a}	0.00841 ± 0.00013^{a}
Vanillin	C	19	0.0032 ± 0.0005^{a}	0.0029 ± 0.0003^{a}	0.001584 ± 0.000015^{a}	0.00141 ± 0.00004^{a}	0.00203 ± 0.00005^{a}
		20	–	0.0025 ± 0.0004^{b}	0.00227 ± 0.00015^{b}	0.00157 ± 0.00008^{a}	–
		21	0.00168 ± 0.00025	–	–	–	–
Total of volatile phenols		19	0.0487 ± 0.0020^{c}	0.0462 ± 0.0006^{c}	0.0389 ± 0.0013^{d}	0.065 ± 0.006^{b}	0.0914 ± 0.0008^{a}
		20	0.01952 ± 0.00013^{a}	0.0451 ± 0.0014^{d}	0.0366 ± 0.0016^{c}	0.0329 ± 0.0023^{b}	0.0318 ± 0.0005^{b}
		21	0.0537 ± 0.00332^{a,b}	0.05738 ± 0.00253^{a}	0.05144 ± 0.00189^{a,b,c}	0.04536 ± 0.003^{c}	0.0505 ± 0.0019^{b,c}
Unknown Compounds							
n.i. (*m/z* 67–82)	–	19	0.0108 ± 0.0003^{c}	0.0094 ± 0.0013^{b,c}	0.01084 ± 0.0005^{c}	0.0080 ± 0.0009^{b}	0.0045 ± 0.0008^{a}
		20	0.377 ± 0.002^{e}	0.1391 ± 0.0022^{d}	0.023 ± 0.003^{a}	0.071 ± 0.010^{c}	0.048 ± 0.006^{b}
		21	0.00711 ± 0.00035^{d}	0.0041 ± 0.00049^{c}	0.00276 ± 0.0001^{a,b}	0.00221 ± 0.00031^{a}	0.00325 ± 0.00026^{b}
n.i. (*m/z* 71–59-43)	–	19	0.00211 ± 0.00010^{a}	0.0033 ± 0.0004^{b}	0.00185 ± 0.00005^{a}	0.00195 ± 0.00012^{a}	0.00201 ± 0.00019^{a}
		20	–	–	–	–	–
		21	0.00148 ± 0.00022^{a}	–	–	0.00168 ± 0.00001^{a}	–
n.i. (*m/z* 72–84-57)	–	19	0.00112 ± 0.00008^{a}	0.0026 ± 0.0003^{c}	0.00142 ± 0.00021^{a,b}	0.00169 ± 0.00014^{a,b}	0.001902 ± 0.000008^{b,c}
		20	–	–	0.00135 ± 0.00014	–	–
		21	–	–	–	0.00165 ± 0.0002	–
n.i. (*m/z* 70–55-43)	–	19	–	0.00196 ± 0.00016	–	–	–
		20	–	–	–	–	–

(*continued on next page*)

Table 1 (*continued*)

		Relative peak area* ± SD†					
Volatile Compounds	ID	Harvest	SC	SELL	SELZ	SEZZ	SE4Z
		21	–	0.00308 ± 0.00046^{a,b}	0.00354 ± 0.00051^{b}	0.00238 ± 0.00035^{a}	–
n.i. (*m/z* 81–67-96–138)	–	19	–	–	0.00089 ± 0.00003^{a}	0.00280 ± 0.00006^{c}	0.00224 ± 0.00014^{b}
		20	–	–	–	–	–
		21	–	–	–	–	–
n.i (*m/z* 55–71-99)	–	19	0.00277 ± 0.00010^{d}	0.00220 ± 0.00012^{c}	0.0016 ± 0.0003^{b}	0.00142 ± 0.00012^{a,b}	0.00103 ± 0.00006^{a}
		20	0.00212 ± 0.00009^{a}	0.0043 ± 0.0004^{c}	0.002978 ± 0.000025^{a,b}	0.00372 ± 0.00003^{b,c}	0.0055 ± 0.0007^{d}
		21	0.0033 ± 0.00042^{b}	–	–	0.00188 ± 0.00028^{a}	–
n.i. (*m/z* 55–71-99)	–	19	0.00179 ± 0.00003^{b}	0.0023 ± 0.0003^{c}	0.00155 ± 0.00015^{b}	0.00115 ± 0.00007^{a}	0.001111 ± 0.000003^{a}
		20	–	–	–	–	–
		21	0.00155 ± 0.00005^{a,b}	–	0.00134 ± 0.00008^{a}	0.00143 ± 0.00021^{a,b}	0.00169 ± 0.00016^{b}
n.i (*m/z* 98–69)	–	19	0.00379 ± 0.00003^{a}	0.0073 ± 0.0011^{c}	0.00450 ± 0.00019^{a,b}	0.0060 ± 0.0009^{b,c}	0.0051 ± 0.0007^{a,b}
		20	–	–	–	–	–
		21	0.0035 ± 0.0003^{c}	0.0028 ± 0.0004^{b,c}	0.0026 ± 0.0003^{a,b}	0.0020 ± 0.0003a	0.00237 ± 0.00005^{b}
n.i (*m/z* 68–59-94)	–	19	–	–	–	0.00483 ± 0.00018	–
		20	–	–	–	–	–
		21	0.001449 ± 0.000012	–	–	–	–
n.i. (*m/z* 70–42)	–	19	0.0091 ± 0.0013^{c}	0.0053 ± 0.0005^{a,b}	0.0041 ± 0.0005a	0.00404 ± 0.00010^{a}	0.0061 ± 0.0009^{b}
		20	–	0.00229 ± 0.00019^{a}	0.0023 ± 0.0003^{a}	–	0.0042 ± 0.0006^{b}
		21	–	–	–	–	–
n.i. (*m/z* 70–98)	–	19	0.0017 ± 0.0003^{a}	0.00385 ± 0.00024^{b,c}	0.0014 ± 0.0003^{a}	0.00320 ± 0.00009^{b}	0.0044 ± 0.0006^{c}
		20	–	–	0.00181 ± 0.00021	–	–
		21	–	–	–	–	–
n.i. (*m/z* 135–150)	–	19	0.0042 ± 0.0005^{a}	–	–	–	0.0020 ± 0.0011^{a}
		20	0.0064 ± 0.0003^{c}	0.0105 ± 0.0011^{e}	0.0042 ± 0.0006^{a}	0.00536 ± 0.00003^{b}	0.00723 ± 0.00012^{d}
		21	–	–	–	–	–
n.i. (*m/z* 135–150)	–	19	0.00160 ± 0.00011^{a}	0.0034 ± 0.0004^{b}	0.00069 ± 0.00010^{a}	0.00110 ± 0.00013^{a}	0.00123 ± 0.00013^{a}
		20	–	–	–	–	–
		21	–	–	–	–	–
n.i. (*m/z* 85)	–	19	0.027 ± 0.004^{b}	0.041 ± 0.005^{c}	0.0194 ± 0.0018^{a}	0.03946 ± 0.00021^{c}	0.0398 ± 0.0015^{c}
		20	–	0.025 ± 0.004^{b}	–	0.0127 ± 0.0006^{a}	–
		21	0.0105 ± 0.0016^{c}	0.00334 ± 0.00015^{a}	0.00255 ± 0.00004^{a}	0.0024 ± 0.0004^{a}	0.0062 ± 0.0009^{b}
Total of unknown compounds		19	0.0660 ± 0.0023^{b}	0.082 ± 0.005^{a}	0.0479 ± 0.0010^{c}	0.0754 ± 0.0023^{a,b}	0.070 ± 0.010^{a,b}
		20	0.389 ± 0.003^{a}	0.188 ± 0.003^{b}	0.041 ± 0.003^{e}	0.099 ± 0.011^{c}	0.070 ± 0.004^{d}
		21	0.0283 ± 0.0019^{a}	0.0133 ± 0.0012^{b}	0.0128 ± 0.0009^{b}	0.0156 ± 0.0003^{b}	0.0135 ± 0.0010^{b}
Totals of volatile compounds		19	9.13 ± 0.21^{b}	11.0 ± 0.3^{a}	9.3 ± 0.6^{a,b}	9.06 ± 0.25^{b}	10.2 ± 1.3^{a,b}
		20	8.616 ± 0.022^{a}	10.0 ± 1.3^{a,b}	12.2 ± 0.4^{c}	10.7 ± 0.6^{b,c}	9.7 ± 0.5^{a,b}
		21	13.91 ± 0.03^{a}	12.1 ± 0.8^{a,b}	11.90 ± 0.19^{b}	10.90 ± 0.24^{b}	12.562 ± 0.010^{a,b}

ID: kind of identification: A, mass spectrum and LRI agreed with standards; B, mass spectrum agreed with mass spectral data base and LRI agreed with the literature data (TI); C, mass spectrum agreed with mass spectral data base. LRI values in Table 3S (supplementary material).
Sample codes of grape musts: SC: conventional vineyard. Organic vineyard: SELL: tillage on both sides of the vines row; SELZ: cover crop on one side and tillage on the other side of the vines row; SEZZ: cover crop on both sides of the vines row, SE4Z: cover crop on two rows on both sides of the sampled row.
n.i.: non-identified compound.
† Similar superscript letter in the same row indicates no significant statistically differences ($p < 0.05$).
* Relative peak area of volatile compounds in 7.5 mL of must.

contributed to the separation between conventional and organic musts from the same harvest, especially in 2019 and 2020 (Fig. 4S). The variable loading showed that most volatile compounds were correlated with samples from the 2019 harvest. Thus, all terpenes, acids, acetic acids esters, and methyl esters were correlated with samples from this harvest. However, the highest number of aldehydes was correlated with samples from the 2021 harvest. Therefore, the PCA results showed an important influence of the harvest on the type of cultivation and this influence is higher for musts from organic cultivation.

Moreover, we have noted different influences on volatile compounds with different aromatic notes, this will provide musts with different aromatic profiles. To delve into these results, volatile compounds were grouped according to their aromatic notes in green-vegetable-mint, floral, fruity, fatty-waxy, balsamic-chemical, sweet-caramel-coffee, nutty, citric, dairy, off-flavour, spicy-toasted, and cheesy-pungent. Aromatic notes of volatile compounds used were those described by Callejón, Morales, Troncoso, and Ferreira (2008), and in several aroma databases (Flavornet and human odor space, 2021; The Good Scents Company Information System, 2021; and The LRI & Odour Database-Odour Data, 2021). The first group included the highest number of compounds and the last the lowest. Subsequently, we added up their relative area values, normalised the resulting values, and represented them as spider graphs for comparison with their hypothetical aromatic profile (Fig. 2). On one hand, the musts from conventional cultivation had similar profiles, the principal difference appearing to be the marked fruity aroma of musts from the 2021 harvest (Fig. 2A). Most aromatic notes presented significant differences for one harvest with respect to the others, except for dairy and cheesy-pungent aromatic notes. On the other hand, the musts from organic cultivations seem to have more different aromatic profiles, showing significant differences in four aromatic notes over the three harvests (Fig. 2B); moreover, those from the 2019 harvest presented a distinctive citric aroma and those from the 2020 harvest a spicy aroma, with those from the 2021 harvest appearing to be less aromatic. If we compare the aromatic profile between crop

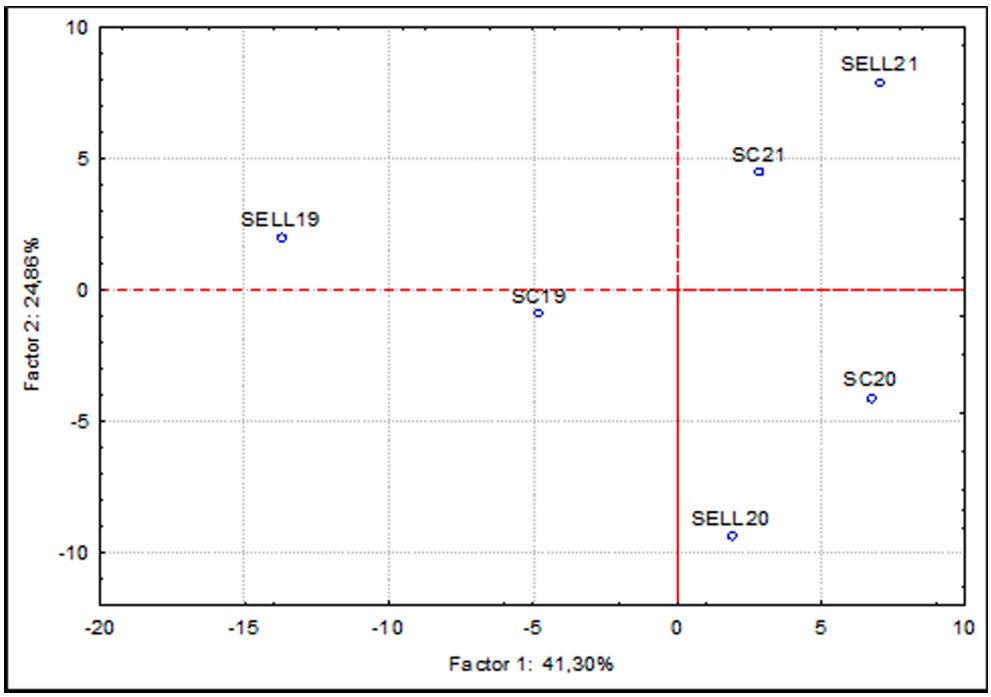

Fig. 1. PCA scores plot of musts from conventional and organic cultivations obtained in the three harvests studied.

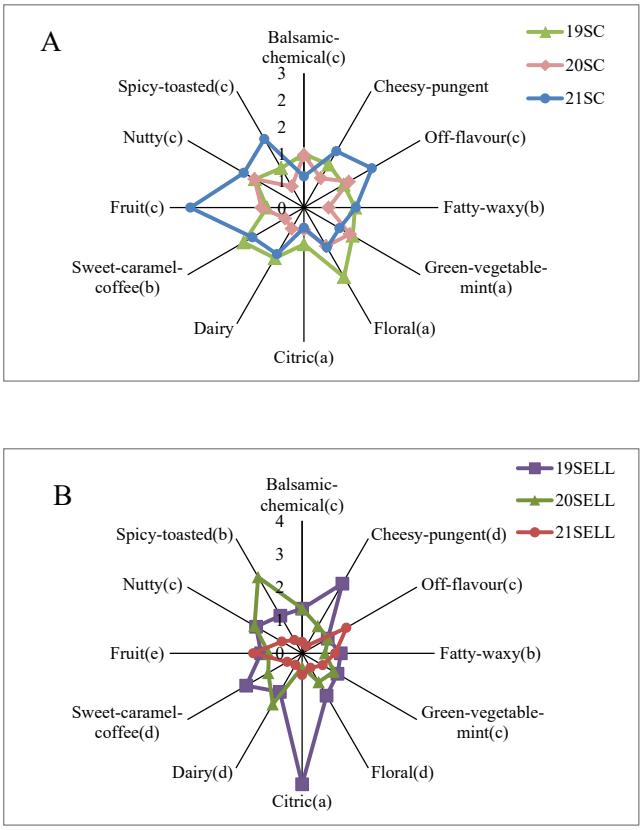

Fig. 2. Spider Chart of hypothetical aromatic profile of musts from conventional (A) and organic cultivations (B). Mean of letter between bracket: a: 2019 harvest value significantly different; b: 2020 harvest value significantly different; c: 2021 harvest value significantly different; d: values of all three harvests significantly different; e: 2020 and 2021 values significantly different; ($p < 0.05$).

types for each harvest (Fig. 5S), we observe higher values in the case of organic than in conventional cultivations, for most aromatic notes, in the 2019 and 2020 harvests (Fig. 5S A and B); however, a contrary trend is observed in the 2021 harvest (Fig. 5S C).

3.2. *Effect of cover crops on organic cultivation*

Different assays to study the influence of Zulla cover crops were performed during three harvests. With regard to the total content of the different chemical groups, we found significant differences only among some kinds of crops in the case of the ethyl esters group and C_{13}-norisoprenoids. Musts obtained from vines cultivated with four lines of Zulla around them (SE4Z) showed the highest amount of ethyl esters total content with significant differences with respect to musts from vines cultivated with only one line of Zulla around them (SELZ). Conversely, the lowest amount of C_{13}-norisoprenoids total content was calculated for SE4Z musts, being significant with respect to SELZ and SEZZ musts.

If we consider the harvest independently, the volatile compounds total content showed a similar trend in the 2019 and 2021 harvests, reaching the highest values in musts from vines with tilled soil (SELL) and SE4Z (Fig. 3). Whilst in the 2020 harvest, this occurred in SELZ and SEZZ musts, although there was only a significant difference in this harvest, in the case of the SELZ sample with respect to the SELL and SE4Z samples and, in the 2019 harvest, between the SELL and SEZZ samples.

A similar trend in the three harvests was observed in the total content of lactones, SELL musts reached the highest amounts, being significantly different in the case of the 2019 and 2020 harvests and SELZ musts the lowest content, only significant for the 2019 harvest. Curiously, if we consider only the musts subjected to the influence of Zulla cover crops (SELZ, SEZZ, and SE4Z), there was a proportional increase in the total amount of lactones as the amount of Zulla cover crop increased, in all three harvests. This fact may be due to γ-butyrolactone and dihydroactinidiolide, the regression coefficients of which were higher than 0.9 with respect to Zulla cover crop proportion, except in the case of the first compound in the 2019 harvest ($R^2 = 0.54$).

Moreover, SELL musts also showed the highest total content of

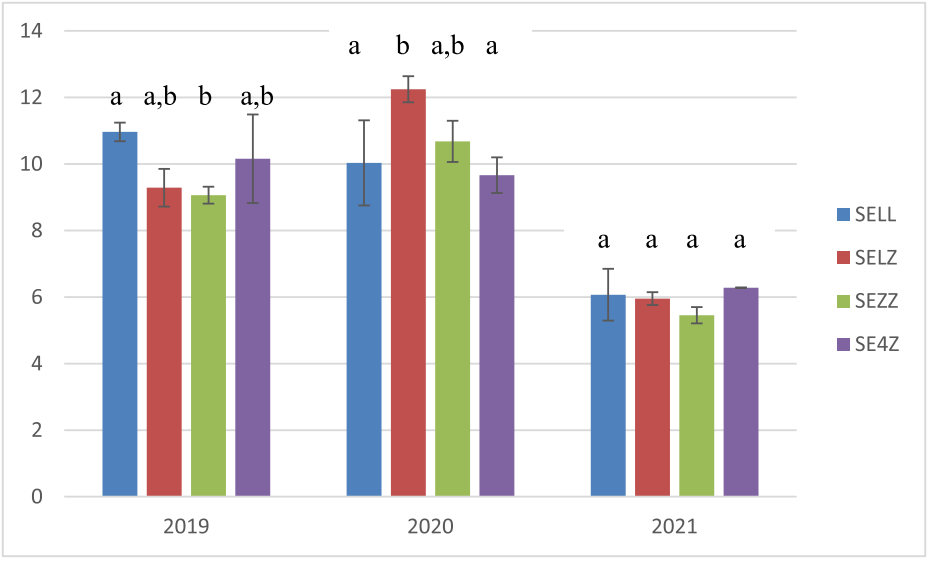

Fig. 3. Total values of relative peak area of all volatile compounds determined in musts from vine cultivation with four different amounts of Zulla cover crop around them (different letters means significant difference, $p < 0.05$).

nitrogen compounds, with significant differences with the rest for the 2019 and 2021 harvests. The SELZ musts showed the lowest total content of unknown compounds, that were significant in the case of the 2019 and 2020 harvests. Finally, SE4Z musts had the lowest C_{13}-norisoprenoids total content, although this was only significant in the 2020 harvest.

For the remaining chemical groups, different trends were observed in all three harvests. Thus, organic musts presented important differences among harvests, for example in the total content of alcohols and aldehydes (Table 1) and this was due to the amounts of C6-alcohols and C6-aldehydes. In our study, most C6-alcohols reached higher amounts in all organic musts in the 2019 and 2020 harvests, observing the lowest differences in the case of hexanol (about double concentration) and the highest in the case of *cis*-2-hexen-1-ol or 1-hexen-3-ol, which was not detected in the 2021 harvest. Conversely, the musts from the 2021harvest reached the highest total content of C6-aldehydes, except for *trans*-2-hexenal, highlighting the concentrations of hexanal and *cis*-2-hexenal in this harvest.

The trend of C6 volatile compounds may be seen easily in the heatmap from cluster analysis (Fig. 6S, supplementary material). Moreover, in most cases, the highest differences of concentrations for C6-aldehydes were observed among the SE4Z musts. The ratio between the relative peak area values of C6-alcohols and their corresponding aldehydes derivate could be pointing out an increased activity of the alcohol dehydrogenase that would be converting these aldehydes to the corresponding alcohols, especially in the case of hexanol/hexanal and *cis*-2-hexenol/*cis*-2-hexenal, in the 2019 and 2020 harvests. Hence, musts from these two harvests could have less of a herbaceous character than those from 2021, since the perception thresholds of C6-alcohols are higher than C6-aldehydes (D'Onofrio, 2011).

Although the contents of C6-compounds have been related to grape variety (Ferreira, López, & Cacho, 2000) and the grape maturation stage (Pedneault, Dorais, & Angers, 2013), we also noted a significant influence of the harvest and to a lesser extent, the amount of Zulla cover crop.

On the other hand, a clear effect of the cover crop was observed in the case of veratrol, a compound only detected in the 2019 harvest; a direct correlation between the amount of this compound and the amount of Zulla was observed ($R^2 = 0.96$). However, for other compounds, these effects were different depending on the harvest, presenting opposite correlations with the amount of Zulla, such as pentanal ($R^2 = 0.73$ in 2019 and R^2 = -0.81 in 2021), 2-methyl-butanal ($R^2 = -0.94$ in 2019 and $R^2 = 0.91$ in 2021), limonene ($R^2 = -0.76$ in 2019 and $R^2 = 0.72$ in 2020), or 1-penten-3-ol ($R^2 = 0.90$ in 2019 and $R^2 = -0.79$ in 2020).

PCA was carried out, a total of 134 volatile compounds were included according to software criterium (variables with a minimum number of cases with values greater than 0, which show variance). The first three principal components (PCs) explained a low percentage of the total variance of the data (68.8%). In Fig. 4, it can be seen how the samples are separated according to their harvests; in particular, PC1 separated the musts from the 2019 and 2021 harvests, and PC2 the musts from the 2020 harvest from musts from the other two harvests. A higher number of variables, 61 volatile compounds, were correlated with samples from the 2020 harvest, among them, most alcohols (20) and ketones (13), and the only two acetic acid esters included in the model (methyl and ethyl acetate). Forty-six volatile compounds were correlated with samples from the 2019 harvest, most terpenes (8), volatile phenols (6) and unknown compounds (9), and the only two C13-norisoprenoinds included as variables. Finally, the harvest correlated with the lowest number of volatile compounds (27) was that of 2021, highlighting a high number of aldehydes (13) and methyl esters (4). This fact showed once again the important influence of the harvest on the volatile profile of the musts studied.

However, when PCA was performed to check if the volatile compounds could group the samples according to cover crop treatment in each harvest independently, a good separation of samples was obtained according to the different soil treatment in the three harvests. In these PCAs, the first three PCs explained the 91.8 %, 90.8%, and 90.9% of the total variance of the data for the 2019, 2020, and 2021 harvests, respectively. In the 2019 and 2020 harvests, the first PC separated the must from vines cultivated in tilled soil (SELL) from those cultivated with different amounts of Zulla cover crop (Figs. 5 and 6). Moreover, the second PC separated the musts from vines cultivated with only one line of Zulla cover crop from those cultivated with more amounts of Zulla cover crop around them, in both harvests. A better separation between SEZZ and SE4Z musts was observed in the 2020 harvest than in the 2019 harvest. In the case of the 2021 harvest, each sample was in a different quadrant (Fig. 7). Thus, as the exposure time to the Zulla cover crop increased, the samples with different degrees of cover crop were better separated. Moreover, considering the variables loadings values, a higher number of volatile compounds was correlated with SELL musts in all harvests, but in 2021, the number was not as high as for the other two harvests. We also observed that several volatile compounds were correlated with the same kind of crop in all three harvests, especially with the SELL samples, such as acetic acid, 1-hexanol, 1-heptanol, 3 and

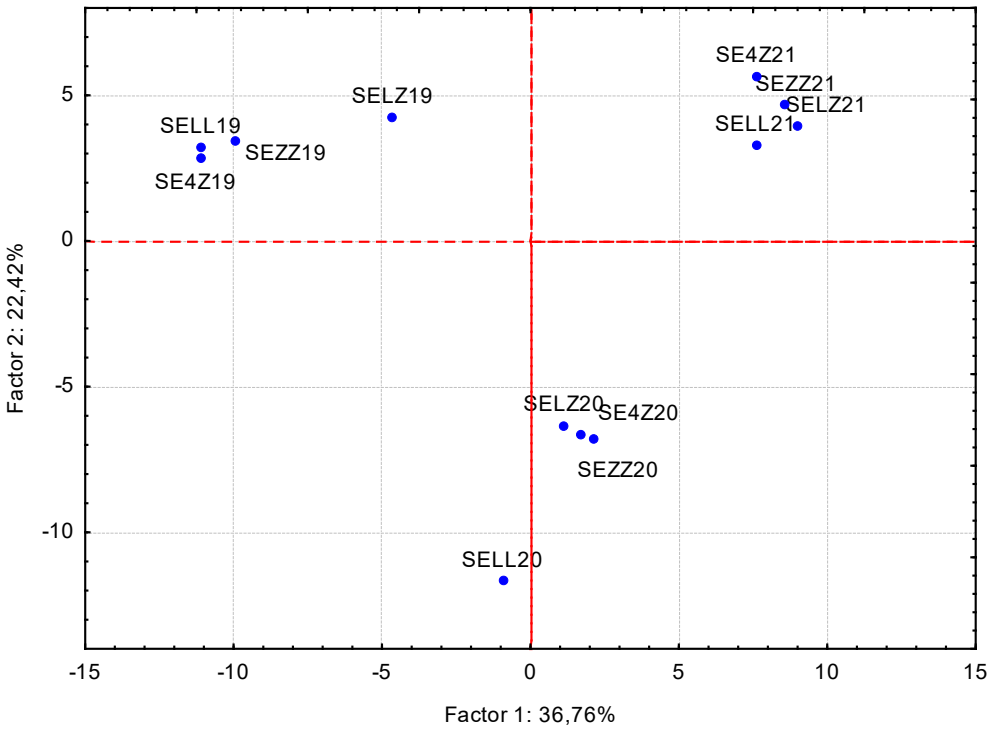

Fig. 4. PCA scores plot of musts from organic cultivation obtained in all three harvests studied.

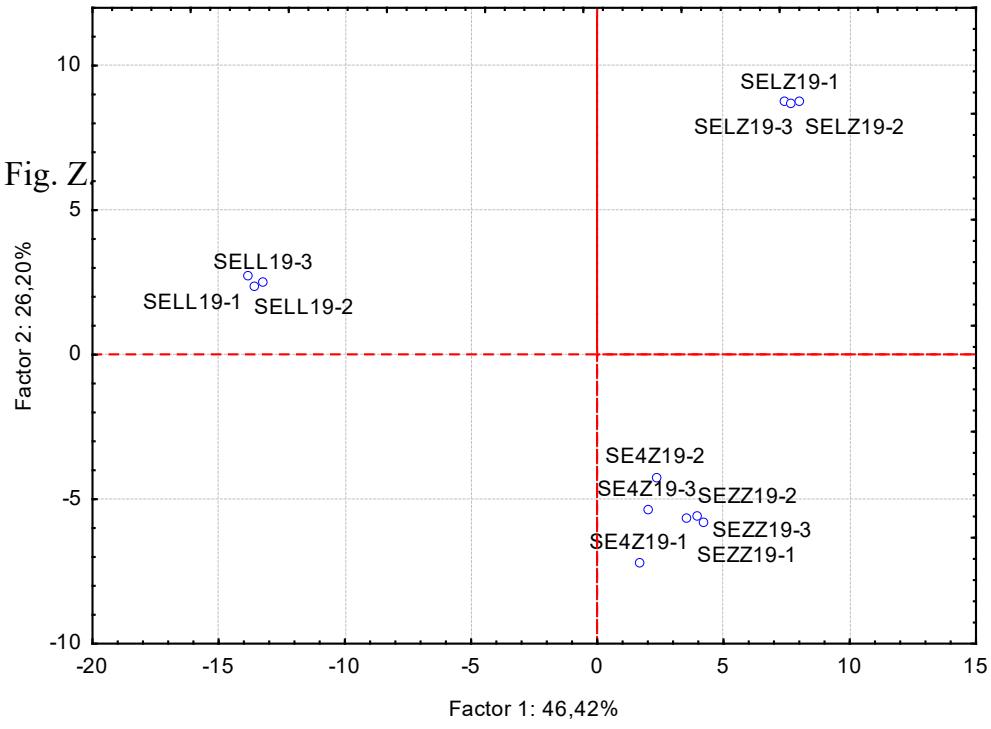

Fig. 5. PCA scores plot of musts from organic cultivation obtained in the 2019 harvest.

2-furfuraldehyde, diacetyl, 6-Methyl-5-hepten-2-one, ɣ-nonalactone, hotrieno, nerol, vanillin among others.

When volatile compounds data was grouped to obtain the hypothetical aroma profile of these musts, differences due to cover crop treatment that were again different in each harvest (Fig. 8) can also be observed. Hence, in the 2019 harvest (Fig. 8A) citric, nutty, fruit, spicy-toasted and off-flavour aromatic notes were significantly higher in musts without cover crop, highlighting the cheese-pungent and dairy notes in musts from vines with the maximum number of lines around them (SE4Z). The musts obtained from vines cultivated without cover crop in the 2020 harvest accounted for the highest values for dairy and sweet-caramel-coffee aromatic notes, and when a large amount of cover crop was used around musts (SEZZ and SE4Z), the musts obtained presented the lowest values for balsamic-chemical, cheese-pungent, and nutty

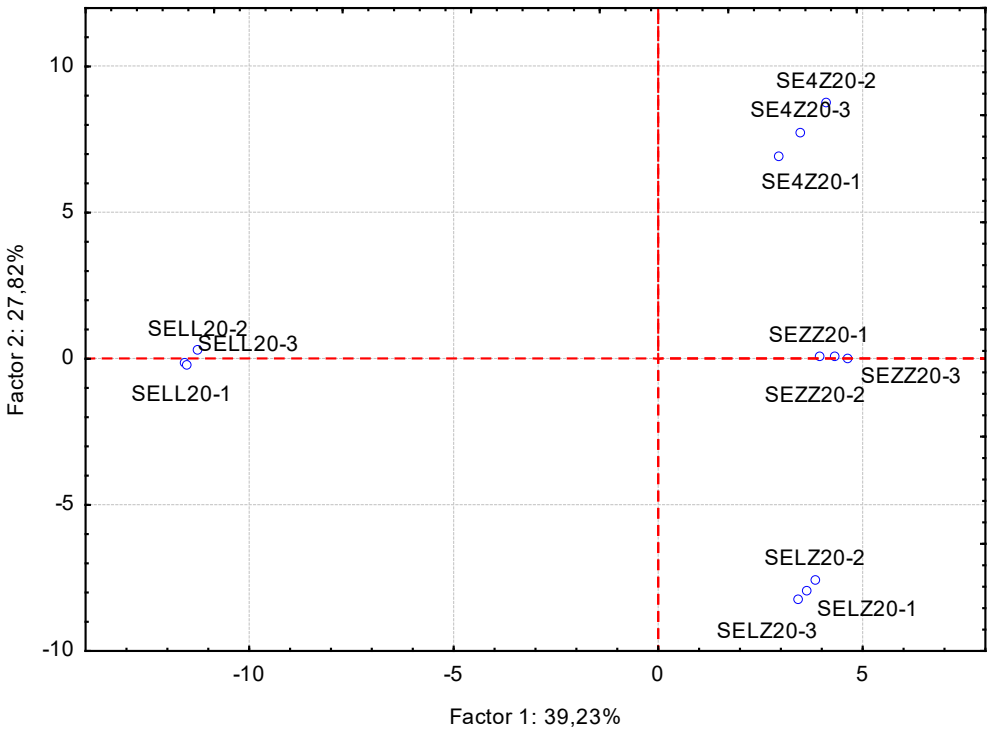

Fig. 6. PCA scores plot of musts from organic cultivation obtained in the 2020 harvest.

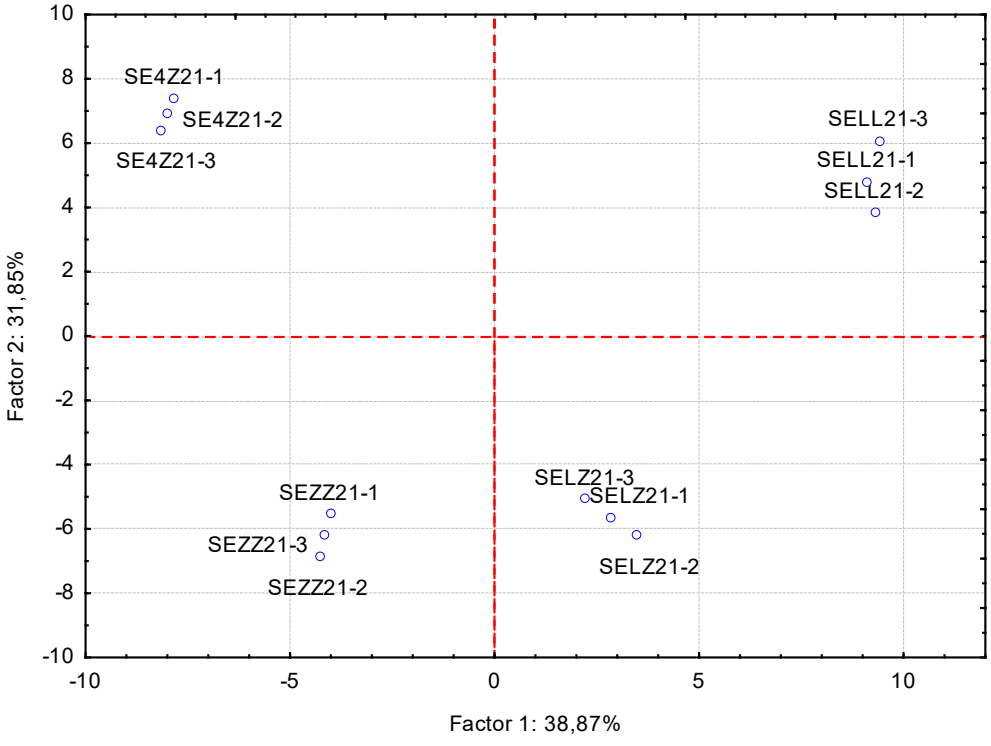

Fig. 7. PCA scores plot of musts from organic cultivation obtained in the 2021 harvest.

notes (the first two could be considered as negative aromas). Moreover, in the case of SE4Z, the sweet-caramel-coffee and spicy-toasted aromas were also significantly lower than in the other musts (Fig. 8B). In the case of the 2021 harvest, a significant increase of balsamic-chemical aroma was observed as the amount of cover crop increased and a contrary trend showed the cheesy-pungent aroma, reaching the highest value in the case of absence of cover. Moreover, these kinds of musts can be highlighted for their citric, sweet-caramel-coffee, and fruit aromatic notes (Fig. 8C).

If we compare the aromatic profile of musts obtained in the different harvests by subjecting vines to the same cover crop treatment (Fig. 7S. Supplementary material), very different aromatic profiles are observed,

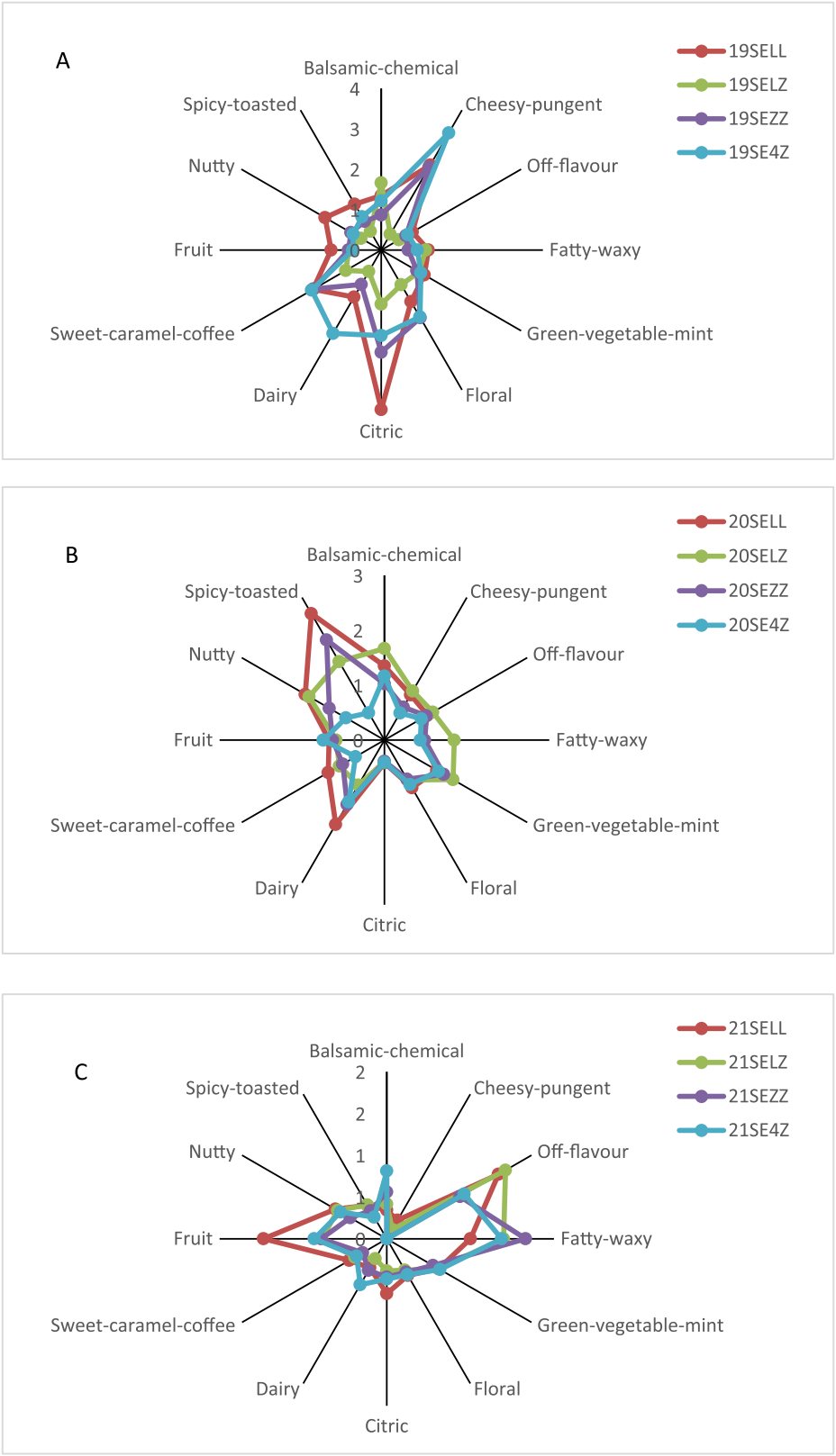

Fig. 8. Spider Chart of hypothetical aromatic profile of musts from cultures with different cover crop treatments: (A) 2019 harvest, (B) 2020 harvest and (C) 2021 harvest.

especially in the case of musts from vines cultivated with one line of Zulla around them (SELZ). Conversely, the most similar musts seem to be those from vines cultivated with the highest amount of Zulla around them, from the 2020 and 2021 harvests. These also showed the lowest values for most aromatic notes.

On the other hand, there are several volatile sulphur compounds associated with typical 'reduced' aromas in wine, such as methanethiol and ethanethiol. Shiraz wines can present this aromatic defect. Bekker, Wilkes, and Smith (2018) showed dimethyl disulphide and methyl thioacetate were important precursors to methanethiol. Dimethyl disulphide was detected in the musts studied except in must from vines cultivated with the highest amount of Zulla cover crop, in the last two harvests. Moreover, an inverse correlation between the amount of this compound and the proportion of Zulla cover crop around the musts was noted. This could indicate that there is a positive effect of Zulla cover crop with regard to this wine off-flavour.

The results showed important differences in volatile and aromatic profiles of the studied musts from the different harvests, highlighting the significant influence exerted by climatic conditions on the composition of secondary grape metabolites. However, the mean temperatures of the three harvests were quite similar and the main difference was the rainfall, being more abundant in 2020 and 2021. as well as showing a different annual rainfall pattern (Fig. 1S. Supplementary material). Thus, the rainiest months were October and November for the 2019 harvest, January and March for the 2020 harvest, and November and January for the 2021 harvest.

Although there seems to be a detriment in the content of volatile compounds due to cover crop in the first harvest, this was gradually lessened in each harvest. Hence, the cover crop may exert a certain negative effect on volatile composition during the first years of implantations due to a possible competition for nutrients or water with the vine, but as time goes on, this negative influence seems to begin to disappear, thanks to the advantages provided by cover crops, as opposed to soil tillage.

4. Conclusions

The influence of different kinds of vineyard cultivation managements on the volatile profile of musts was studied. The results showed that the effect of the harvest on must volatile composition is more important than agronomic practices during the three years studied. Zulla cover crop did not produce negative effects on volatile profile with respect to conventional or organic cultivation with soil tillage. Therefore, organic cultivation using Zulla cover crop, during the months before the sprouting of the vine, is a suitable tool for the implementation of friendly ecosystem management in a warm climate Syrah vineyard. Further studies to assess the longer-term effect could be performed.

CRediT authorship contribution statement

E. Valero: Conceptualization, Methodology, Investigation, Writing – original draft, Supervision, Project administration, Funding acquisition. **F. Arranz:** Investigation, Formal analysis, Writing – original draft. **B.J. Moyá:** Investigation, Formal analysis, Writing – original draft. **S. Cruz:** Investigation, Writing – review & editing. **B. Puertas:** Conceptualization, Methodology, Resources, Writing – review & editing, Project administration, Funding acquisition. **M.L. Morales:** Methodology, Formal analysis, Resources, Writing – original draft, Writing – review & editing, Visualization, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was funded by the Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA) through the Project "Investigación e Innovación Tecnológica en Vitivinicultura" (PR.AVA. AVA2019.016) and the European Rural Development Fund (ERDF, EU); and by the European Regional Development Fund (FEDER) and by the Consejería de Economía, Conocimiento, Empresas y Universidad, of Junta de Andalucía, within the framework of the Andalusian FEDER operational program 2014-2020. Specific objective 1.2.3. «Promotion and generation of frontier knowledge and knowledge lead to the challenges of society, development of emerging technologies» within the framework of the reference research project (FEDER-UPO 1381315). FEDER co-financing percentage 80%. Authors would also like to thank the financial aid from the VI Own Research and Transfer Plan of the University of Seville.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodres.2022.111694.

References

Abad, J. H., de Mendoza, I., Marín, D., Orcaray, L., & Gonzaga Santesteban, L. (2021). Cover crops in viticulture. A systematic review (2): Implications on vineyard agronomic performance. *OENO One, 55*(2), 1–27. https://doi.org/10.20870/oeno-one.2021.55.2.4481

Abad, J., Marín, D., Santesteban, L. G., Cibriain, J. F., & Sagüés, A. (2020). Under-vine cover crops: Impact on weed development, yield and grape composition. *OENO One, 4*, 975–983. https://doi.org/10.20870/oeno-one.2020.54.4.4149

Alem, H., Rigou, P., Schneider, R., Ojeda, H., & Torregrosa, L. (2019). Impact of agronomic practices on grape aroma composition: A review. *Journal of the Science of Food and Agriculture, 99*, 975–985. https://doi.org/10.1002/jsfa.9327

Amerine, M. A., & Winkler, A. J. (1944). Composition and quality of musts and wines of California grapes. *Hilgardia, 15*(6), 493–675. https://doi.org/10.3733/hilg.v15n06p493

Antalick, G., Šuklje, K., Blackman, J. W., Meeks, C., Deloire, A., & Schmidtke, L. M. (2015). Influence of grape composition on red wine ester profile: Comparison between cabernet sauvignon and Shiraz cultivars from Australian Warm Climate. *Journal of Agriculture and Food Chemistry, 63*, 4664–4672. https://doi.org/10.1021/acs.jafc.5b00966

Bekker, M. Z., Wilkes, E. N., & Smith, P. A. (2018). Evaluation of putative precursors of key 'reductive' compounds in wines post-bottling. *Food Chemistry, 245*, 676–686. https://doi.org/10.1016/j.foodchem.2017.10.123

Bouzas-Cid, Y., Trigo-Córdoba, E., Orriols, I., Falqué, E., & Mirás-Avalos, J. M. (2018). Influence of soil management on the red grapevine (*Vitis vinifera L.*) Mencía must amino acid composition and wine volatile and sensory profiles in a humid region. *Beverages, 4*, 76. https://doi.org/10.3390/beverages4040076

Callejón, R. M., Morales, M. L., Troncoso, A. M., & Ferreira, A. C. S. (2008). Targeting key aromatic substances on the typical aroma of sherry vinegar. *Journal of Agricultural and Food Chemistry, 56*, 6631–6639.

Chong, J., & Xia, J. (2018). MetaboAnalystR: An R package for flexible and reproducible analysis of metabolomics data. *Bioinformatics, 27*, 4313–4314.

Coletta, A., Toci, A. T., Pati, S., Ferrara, G., Grieco, F., Tufariello, M., & Crupi, P. (2021). Effect of soil management and training system on Negroamaro wine aroma. *Foods, 10*, 454. https://doi.org/10.3390/foods10020454

Delpuech, X., & Metay, A. (2018). Adapting cover crop soil coverage to soil depth to limit competition for water in a Mediterranean vineyard. *European Journal of Agronomy, 97*, 60–69. https://doi.org/10.1016/j.eja.2018.04.013

D'Onofrio, C. (2011). Caratterizzazione funzionale della biosintesi degli aromi durante lo sviluppo dell'acino e controllo della qualità aromatica delle uve. *Italus Hortus, 18*(1), 39–61.

Dötterl, S., & Jurgens, A. (2005). Spatial fragrance patterns in flowers of Silene latifolia: Lilac compounds as olfactory nectar guides? *Plant Systematics and Evolution, 255*, 99–109. https://doi.org/10.1007/s00606-005-0344-2

Ferreira, V., López, R., & Cacho, J. F. (2000). Quantitative determination of the odorants of young red wines from different grape varieties. *Journal of the Science of Food and Agriculture, 80*, 1659–1667. https://doi.org/10.1002/1097-0010(20000901)80:11<1659::AID-JSFA693>3.0.CO;2-6

Flavornet and human odor space by Acree T. & Arn H. Available from https://www.flavornet.org/ October 2021.

Guilpart, N., Roux, S., Gary, C., & Metay, A. (2017). The trade-off between grape yield and grapevine susceptibility to powdery mildew and grey mould depends on inter-annual variations in water stress. *Agricultural and Forest Meteorology, 234–235*, 203–211. https://doi.org/10.1016/j.agrformet.2016.12.023

Kazakou, E., Fried, G., Richarte, J., Gimenez, O., Violle, C., & Metay, A. (2016). A plant trait-based response-and-effect framework to assess vineyard interrow soil

management. *Botany Letters, 163*(4), 373–388. https://doi.org/10.1080/23818107.2016.1232205

Linares Torres, R., De La Fuente Lloreda, M., Junquera Gonzalez, P., Lissarrague Garcia-Gutierrez, J. R., & Baeza Trujillo, P. (2018). Effect of soil management strategies on the characteristics of the grapevine root system in irrigated vineyards under semi-arid conditions. *Australian Journal of Grape and Wine Research, 24*(4), 439–449. https://doi.org/10.1111/ajgw.12359

Luo, J., Brotchie, J., Pang, M., Marriott, P. J., Howell, K., & Zhang, P. (2019). Free terpene evolution during the berry maturation of five *Vitis vinifera* L. Cultivars. *Food Chemistry, 299*(125101), 1–13.

Morales, M. L., Fierro-Risco, J., Ríos-Reina, R., Ubeda, C., & Paneque, P. (2019). Influence of *Saccharomyces cerevisiae* and *Lachancea thermotolerans* coinoculation on volatile profile in fermentations of a must with a high sugar content. *Food Chemistry, 276*, 427–435.

OIV. (2017). Focus OIV. Distribution of the World's Grapevine Varieties in 2015. Available from https://www.oiv.int/public/medias/5888/en-distribution-of-the-worlds-grapevine-varieties.pdf.

OIV. (2021). Focus OIV. The world organic vineyard. 29 Septembre 2021 — Organic viticulture is gaining terrain. Available from https://www.oiv.int/en/viticulture/organic-viticulture-is-gaining-terrain.

Pedneault, K., Dorais, M., & Angers, P. (2013). Flavor of cold-hardy grapes: Impact of berry maturity and environmental conditions. *Journal of Agriculture and Food Chemistry, 61*, 10418–10438. https://doi.org/10.1021/jf402473u

Peñín, J., & Diez, R. (1997). *Cepas del mundo*. Madrid: Pi & Erre.

Ribéreau-Gayon, P., Glories, Y., Maujean, A., & Dubourdieu, D. (2006). *Handbook of enology, the chemistry of wine stabilization and treatments*. Chichester: John Wiley & Sons Ltd..

Tava, A., Biazzi, E., Ronga, D., Mella, M., Doria, F., D'Addabbo, T., … Avato, P. (2021). Chemical identification of specialized metabolites from sulla (Hedysarum coronarium l.) collected in southern Italy. *Molecules, 26*(15), 4606. https://doi.org/10.3390/molecules26154606

The Good Scents Company Information System. Available from http://thegoodscentscompany.com/odor/acetic.html. October 2021.

The LRI & Odour Database - Odour Data by Mottram, R. Available from https://www.odour.org.uk. October 2021.

Ubeda, C., Callejón, R. M., Troncoso, A. M., Peña-Neira, A., & Morales, M. L. (2016). Volatile profile characterisation of Chilean sparkling wines produced by traditional and Charmat methods via sequential stir bar sorptive extraction. *Food Chemistry, 207*, 261–271. https://doi.org/10.1016/j.foodchem.2016.03.117

Wood, C., Siebert, T. E., Parker, M., Capone, D. L., Elsey, G. M., Pollnitz, A. P., et al. (2008). From Wine to Pepper: Rotundone, an Obscure Sesquiterpene, Is a Potent Spicy Aroma Compound. *Journal of Agriculture and Food Chemistry, 56*(10), 3738–3744. https://doi.org/10.1021/jf800183k

Xi, Z.-M., Tao, Y.-S., Zhang, L., & Li, H. (2011). Impact of cover crops in vineyard on the aroma compounds of Vitis vinifera L. cv Cabernet Sauvignon wine. *Food Chemistry, 127*, 516–522. https://doi.org/10.1016/j.foodchem.2011.01.033

Zito, P., Scrima, A., Sajeva, M., Carimi, F., & Dötterl, S. (2016). Dimorphism in inflorescence scent of dioecious wild grapevine. *Biochemical Systematics and Ecology, 66*, 58–62. https://doi.org/10.1016/j.bse.2016.03.003