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Volatilomics analysis of table olive ‘Bella di Cerignola' PDO and associated brines: a case study on different fermentation styles and olive sizes

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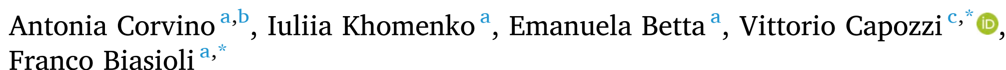

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ABSTRACT

The present study provides the comprehensive volatilomic characterisation of *Olea europaea* L. *cv. Bella di Cerignola* Protected Designation of Origin (PDO) table olives and their associated brines by integrating Proton Transfer Reaction–Time-of-Flight Mass Spectrometry (PTR-ToF-MS) with Gas Chromatography–Mass Spectrometry (GC–MS). In particular, this work aimed to evaluate how fermentation style (Natural/Greek, NAT; *Sivigliano*/Spanish, SIV) and fruit size influence Volatile Organic Compounds (VOCs) associated with these fermented products, with particular focus on microbial metabolic markers. PTR-ToF-MS analysis detected 296 mass peaks, of which 145 significantly differed from blanks. Principal Component Analysis revealed a clear discrimination between NAT and SIV samples, with fermentation style emerging as the dominant source of variance, whereas fruit size had a negligible impact. NAT fermentation, which proceeds spontaneously through brining (10 % NaCl), displayed a markedly richer and more heterogeneous volatilome than the alkali-treated SIV process (2 % NaOH), including also a few volatiles potentially associated with spoilage phenomena. Among the key volatile markers majorly associated with NAT fermentation, such as ethanol, acetaldehyde, acetic acid, propionic acid, and ethyl esters, indicated active alcoholic, heterolactic, and propionic fermentations, predominantly in NAT samples. Additional compounds, such as 3-hexen-1-ol, cyclohexanol, and phenylethyl alcohol, suggested lipoxygenase-like and yeast-associated metabolic pathways. The brines were found to be much richer in volatile compounds, an aspect of potential interest also in the management of these matrices. The combined PTR-ToF-MS and GC–MS approach proved decisive for both rapid, non-invasive screening and robust compound identification, interesting also for future studies, to exploit the potential of the analytical technique for green chemical analysis, massive screenings, and real-time studies. This study presents a methodological update for volatilomic monitoring of complex plant-based fermented foods, highlighting the link between metabolic diversity, fermentative processes and sensory potential in traditional table olive production.

1. Introduction

Table olives are among the most widely consumed fermented vegetables in the Mediterranean region, and their global popularity is increasing due to their nutritional and functional properties, which are attributed to the presence of polyphenols, vitamins, minerals, and fatty acids [1,2]. These fermented vegetables are produced worldwide, with Spain as the market leader in production, followed by Italy and other Mediterranean countries such as Greece, Algeria, Turkey, Egypt, and Portugal. According to the International Olive Oil Council (IOOC) five main traditional methods are used for their production: *(i)* the treated olives or Spanish style, *(ii)* the natural olives or Greek style, *(iii)* the olives darkened by oxidation or Californian style, *(iv)* dehydrated /shriveled olives, and *(v)* other methods based on local practices [3,4]. Various factors significantly influence the organoleptic characteristics of the final product [5], including NaCl content, processing temperature, and the origin of the olives, which affects the dominant microbiota during fermentation [6]. Unlike other fermented products, the fermentation of table olives is challenging to control because the raw material can not be thermally treated [1,2]. As a result, salt is added to reduce

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water activity, prevent the growth of spoilage microorganisms, and improve the taste and texture of the final product [7]. Another strategy of great interest to industries is developing effective starter cultures to reduce the probability of spoilage and help to achieve an improved and more predictable fermentation process [8,9]. Table olive fermentation is a complex and time-consuming process influenced by multiple interacting factors. Recently, the rapid advancement of omics technologies has provided a significant opportunity to understand better microbial diversity, adaptation, and functionality in complex ecosystems [10]. While metabolomics generally focuses on non-volatile metabolites, volatile organic compounds (VOCs) remain an underexplored aspect of microbial metabolism in multi-omics studies [11]. VOCs, however, have the advantage of providing a dynamic, real-time snapshot of metabolic activity, as opposed to the more static insights obtained from other omics approaches. Numerous studies have investigated the volatilome of olive table and particularly olive oil due to the critical role of aroma and flavour. It is well established that the olive cultivar, geographic origin, ripening stage at harvest, and processing methods all affect the volatile profile [12]. These characteristics have been explored for authenticity and traceability purposes, using a variety of traditional analytical techniques. Among them, isotope ratio analyses, such as isotopic ratio mass spectrometry (IRMS) and site-specific natural isotope fractionation nuclear magnetic resonance (SNIF-NMR), have proven valuable in verifying origin and authenticity [13]. In addition, other analytical platforms have been applied to determine the geographical origin of food products, including gas chromatography–mass spectrometry (GC–MS), dynamic headspace gas chromatography (DHS-GC), solid-phase microextraction (SPME) coupled with GC–MS or GC-flame ionization detector (GC-FID), high-performance liquid chromatography (HPLC), and electronic nose systems [14]. Beyond authenticity studies, some works have addressed the selection of starter cultures to standardise the table olive fermentation process [15]. Yet, due to the complexity and variability of microbial ecosystems, this approach remains difficult to scale. As a result, some researchers have begun characterising the microbial communities and associated volatilomic profiles of table olives as a tool to support the selection and development of tailored starter cultures [1]. However, many of these analytical techniques are either too time-consuming to allow high-throughput screening or lack the sensitivity and resolution required to detect meaningful differences between samples. In this context, rapid VOC analysis techniques are particularly attractive. For example, Masi et al. [16] applied Proton Transfer Reaction–Time-of-Flight Mass Spectrometry (PTR-ToF-MS) for in vivo VOC analysis in olive fruit samples. Their goal was to explore the technique's potential in discriminating olive cultivars and ripening stages, and in identifying key compounds involved in fruit maturation. Taiti et al. [17] investigated the VOC profile of fifteen olive Italian cultivars using the same technique to understand their impact on olive oil production. Overall, studies on olive fruit with PTR-MS remain very limited, with most research focusing instead on the analysis of volatiles in olive oils, as mentioned earlier [12,18,19].

Our study addresses a distinct objective: evaluating the capacity of VOC profiling to distinguish between different fermentation styles,olive sizes and their respective brines, and to identify key volatile markers at the end of the fermentation process. While previous studies have suggested that some morphological traits of olives can influence VOC profiles [20], a direct analysis of fruit size as a factor affecting volatile composition has not been reported, making this aspect a novel focus of our work. To achieve this goal we integrated two complementary analytical approaches, PTR-ToF-MS and GC–MS, which differ significantly in methodology but share the common objective of VOC analysis. GC–MS is a well-established, reference technique in volatilomics, capable of quantifying and identifying compounds using standards and retention time libraries [21]. Additionally, it enables the resolution of isomers and, when enantioselective stationary phases are employed [22], the separation of molecular enantiomers, thereby providing high confidence in compound identification. In contrast, PTR-ToF-MS, increasingly applied in food science [23], is a high-sensitivity analyser capable of acquiring full *m/z* spectra at the microsecond scale, with a typical output time resolution of 1 s [24]. It offers sufficient mass-resolving power to distinguish compounds isobars. However, it does not provide the same level of structural identification as GC–MS. The optimal approach is to combine these two techniques, leveraging the rapid acquisition and high temporal resolution of PTR-ToF-MS alongside the more accurate compound identification capabilities of GC–MS [25]. The novelty of this study lies in three aspects: i) the first integrated analysis combining PTR-ToF-MS and GC–MS data in fermented table olives, both fruits and brines; ii) the first application of PTR-ToF-MS to olive brines; and iii) the first comprehensive evaluation of volatile profile using PTR-ToF-MS and GC–MS, comparing two fermentation styles (Greek and Spanish style),fruit sizes and their brines in cv. *Bella di Cerignola* olives (cultivar at the basis of the fermented table olive Geographical Indication *Bella della Daunia*).

2. Materials and methods

2.1. Plant material

Olives used in our study belong to Apulia cultivar *Bella di Cerignola*, of two different sizes (G = 71–80 pieces/kg, M = 91–120/121–180 pieces/kg) were subjected to two fermentation modes: SIV (*Sivigliano*, Spanish style) and NAT (*Naturale*, Greek/Natural style) (Table 1). For the SIV process (Spanish-style), olives were subjected to an initial alkaline debittering treatment using approximately 2 % (w/v) sodium hydroxide (NaOH) solution for about 12 h. Following alkaline treatment, olives were thoroughly washed with potable water to remove residual NaOH. The treated olives were then transferred into fermentation vessels containing brine with an initial NaCl concentration of approximately 10 % (w/v). In the NAT process (natural/Greek-style), olives were immersed directly in brine without prior chemical debittering. Debittering occurred through spontaneous fermentation driven by the indigenous microbiota naturally present on the fruit surface. Fermentation began with an initial brine NaCl concentration of approximately 10 % (w/v). For both methods, during the first days of fermentation, a rapid decrease in salt concentration was observed due to osmotic exchanges between the brine and olive tissues, after which salinity gradually stabilised. At the end of fermentation, the brine NaCl concentration was approximately 5.5 %, while olives typically reached a salt content of approximately 7 %. The pH progressively decreased during lactic fermentation and was considered stable when values consistently dropped below 4.5. Final titratable acidity, expressed as citric acid monohydrate, was approximately 0.22 %. The samples were taken for analysis after 3 months.

The samples (Table 1) were triturated and mixed with an antioxidant solution consisting of 0.25 g citric acid, 0.25 g ascorbic acid, 50 g water, and 20 g NaCl. Then, 3 g of table olives and 3 mL of brine were

Table 1
Apulia cultivar "Bella di Cerignola" table olives of two different sizes (G = 71–80 pieces/kg, M = 91–120/121–180 pieces/kg) produced with two different fermentation modes: SIV (Sivigliano, Spanish style) and NAT (Naturale, Greek/, Natural style).

Fermentation mode	Matrix	Size (pieces/kg)	Sample name
SIV	olive fruit	M (91–120/121–180)	**M_SIV**
	brine	-	**WM_SIV**
	olive fruit	G (71–80)	**G_SIV**
	brine	-	**WG_SIV**
NAT	olive fruit	M (91–120/121–180)	**M_NAT**
	brine	-	**WM_NAT**
	olive fruit	G (71–80)	**G_NAT**
	brine	-	**WG_NAT**

separately poured into 20 mL vials and closed with a screw cap featuring a silicon/PTFE septum. After being stored at 4 °C overnight, the samples were analysed in triplicate to determine the volatile profiles of the matrices and their respective brines using PTR-ToF-MS and GC–MS.

2.2. Volatile organic compound (VOC) determination using proton transfer reaction time of flight mass spectrometry (PTR-ToF-MS)

A multifunctional autosampler (Gerstel, Mülheim an der Ruhr, Germany) was loaded with three replicates of samples prepared as described in Section 2.1. Headspace measurements of each vial were performed using a commercial PTR-ToF-MS 8000 apparatus from Ionicon Analytik GmbH (Innsbruck, Austria), as previously described by [26]. The ionisation conditions in the drift tube involved 110 °C, 2.80 mbar drift pressure, 624 V drift voltage with an active RF mode and H3O+ as reagent ion. This led to an E/N ratio of about 140 Townsend (1 Td = 10^{-17} V cm^2), where E corresponds to the electric field strength and N to the gas number density. The parameter E/N influences fragmentation and clustering, making it important to work within a range of 120–140 Td [27]. The sampling time per channel of ToF acquisition was 0.1 ns, amounting to 350,000 channels for a mass spectrum ranging up to m/z = 340, which resulted in the acquisition rate of 1 spectrum/s. Each measurement was conducted automatically using a multipurpose GC automatic sampler (Gerstel GmbH, Mulheim am Ruhr, Germany), with an interval of 60 s between measurements to prevent memory effects/carryover. The sample headspace was withdrawn with a 2.5 mL syringe (CTC Analytics AG, Zwingen, Switzerland) and injected into the static headspace (SHS) module (Ionicon Analytik GmbH, Innsbruck, Austria). The flow of zero air inside the static headspace module was 90 sccm, and the syringe was injected at a speed of 30 μL/s, which resulted in a 16-fold dilution of the sample. The injection time was 25 s/sample [26].

2.3. VOC Determination using gas chromatography mass spectrometry (GC–MS)

GC–MS analysis was performed to aid in the identification of VOCs, extracted using headspace solid-phase microextraction (HS-SPME) with a 2 cm fibre coated with 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS, Supelco, Bellefonte, PA, USA). The fibre was exposed to the headspace for 45 min at 37 °C. The compounds absorbed by the SPME fibre were desorbed at 250 °C in the GC injection port for 5 min. The GC was interfaced with a mass detector operating in electron ionisation (EI) mode (internal ionisation source; 70 eV) with a scan range of m/z 33–350 (GC–MS Clarus500, PerkinElmer, Norwalk, CT, USA). Separation was carried out in an HPINNOWax fused silica capillary column (30 m, 0.32 mm ID, 0.5 μm film thickness; Agilent Technologies, Palo Alto, CA, USA). The carrier gas was helium at a constant flow rate of 2.0 mL/min. The oven temperature was programmed as follows: 40 °C (1 min)//5 °C min − 1//250 °C (2 min). Compound identification was based on mass spectral matching with the NIST 14 and Wiley 7th Mass Spectral Libraries, and linear retention indices (LRI) were compared with the literature. LRIs were calculated under the same chromatographic conditions after injection of a C7–C30 nalkane series (Supelco, Bellefonte, PA, USA).

2.4. PTR-ToF-MS data processing and statistical analysis

The internal calibration of mass spectral data and peak extraction were performed according to the procedure described by Cappellin et al. [28]. Peak intensity in ppbv was estimated using the formula [27] described using a constant value for the reaction rate coefficient (k = 2 × 10^{-9} cm^3 s^{-1}). This approach introduces a systematic error in the absolute concentration of each compound, which, in most cases, is below 30 % and could be accounted for if the actual rate constant coefficient were available [29]. All data detected and recorded by the PTR-ToF-MS were processed using MATLAB (MathWorks, Natick, MA, USA). A total of 296 mass peaks were extracted, ranging from m/z 21 to m/z 300. Missing values were imputed with a random value between 0 and the corresponding minimum value. A one-way analysis of variance (ANOVA) was conducted to statistically identify mass peaks that were significantly different (p-value < 0.001) from those in the blank samples (see Table S1 in the Supplementary Materials). Mass assignment was performed, after removing water clusters and isotopes, to derive molecular formulas for the detected mass peaks, using the "Elemental composition calculator" and "Molecular weight calculator" provided with the PTR-ToF-MS software. Tentative identification was based on GC–MS data, the master compound assignment guide from Yáñez-Serrano et al. [30] and the literature related *cv. Bella di Cerignola* or, when not available, concerning the table olives in general. Before performing principal component analysis (PCA), the processed dataset was log-transformed to account for the expected non-normal distribution of metabolomics data. Subsequently, each variable was mean-centred and scaled to unit variance to ensure that all variables contributed equally to the analysis. Based on the PCA results, another ANOVA was applied to determine the mass peak difference between the two types of fermentation. From the selected mass peaks that showed significant differences, only those with confirmed identification were included in the heatmap to enhance the biological relevance and interpretability of the results. Statistical analysis and data visualisation were performed with custom R scripts (version 4.3.2, R Foundation for Statistical Computing, Vienna, Austria) and the external packages “mixOmics”, “ggplot2” and “agricolae”.

3. Results and discussion

Proton Transfer Reaction–Time of Flight–Mass Spectrometry (PTR-ToF-MS) was applied to obtain a rapid and comprehensive volatile profile of the Apulian table olive cultivar *Bella di Cerignola*, one of the most commercially important Italian table olive cultivars, recognised as Protected Designation of Origin (PDO). To the best of our knowledge, this is the first study to employ this technique in characterising volatilomics for both fermented olives and the associated brines, utilising two different fermentation styles. In particular, the olives are traditionally processed using two fermentation styles: *Sivigliano*/Spanish (SIV) and Naturale/Greek (NAT), and are categorised by fruit size into two classes, G (71–80 olives kg^{-1}) and M (91–120 or 121–180 olives kg^{-1}). Both the studied fermentation methods (i.e., SIV, NAT) aim to reduce the natural bitterness of table olives, primarily caused by oleuropein, and to protect the product from microbial spoilage [31]. Furthermore, the different treatments included in the two processes can lead to the selection of distinct microbial communities, which can markedly influence product quality, including microbial metabolites linked with sensory attributes, particularly the modulation of volatile compounds analysed in this study. Analysis of the PTR-ToF-MS mass spectra from the headspace of the samples yielded 296 mass peaks. Of these, 145 peaks were significantly different from the blank (p < 0.001) after excluding isotopes and water clusters (Table S1, Supplementary Materials). These 145 peaks were subsequently used for principal component analysis (PCA), which revealed that the first two principal components (PC1 and PC2) explained approximately 82 % of the total variance (Fig. 1). The loading plot (Fig. 2) illustrates the contribution of individual volatile organic compounds (VOCs) to the explained variance and their influence on the main differentiation trends. In the PCA score plot, circular markers denote samples fermented according to the Sivigliano/Spanish (SIV) method, while triangular markers correspond to those produced by the Naturale/Greek (NAT) process. Each olive sample and its corresponding brine are represented with the same colour hue, differing only in shade intensity. In detail, M and G samples are represented with a lighter shade, while WM and WG (the brines) are shown in a darker shade of the same colour. Marker size indicates fruit category, with larger symbols representing G-sized olives and smaller ones representing M-sized olives. The plot clearly separates samples according to

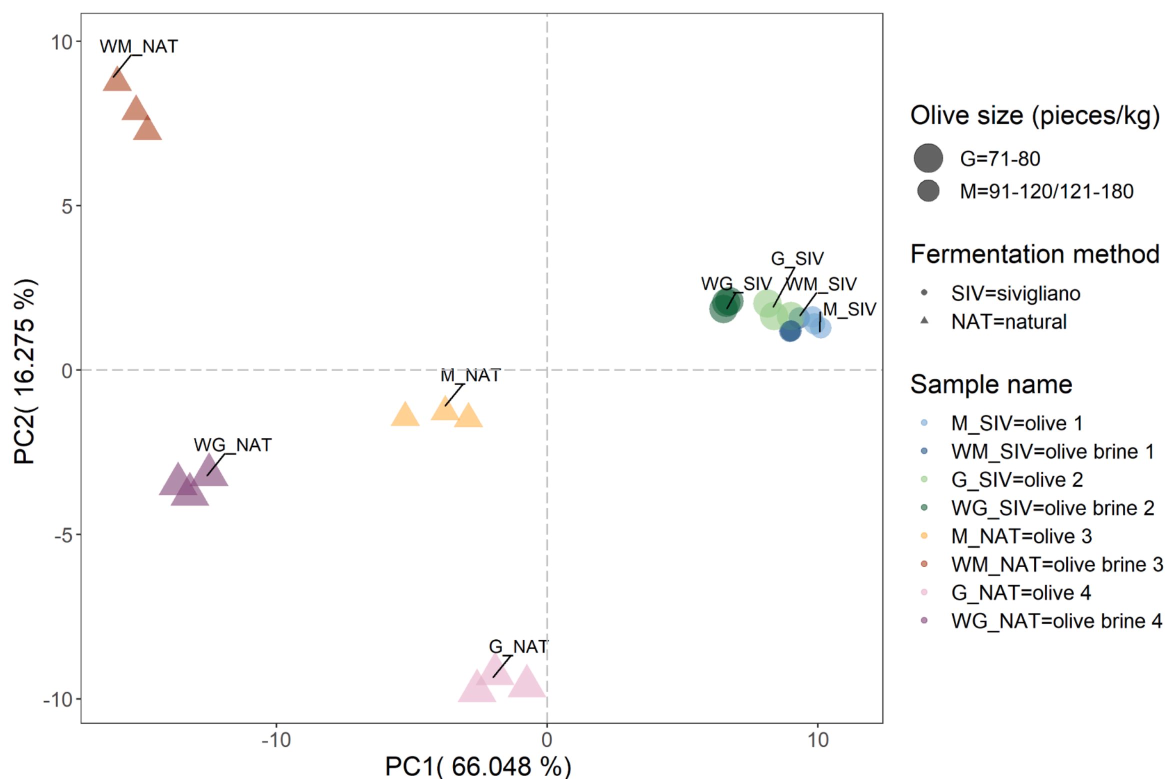

Fig. 1. Principal Component Analysis (PCA) plot based on the volatile metabolome of table olives (G and M) and brines (WG and WM). Samples are grouped by fermentation method (natural vs. sivigliano) and olive size (pieces/kg), as indicated by shape and point size, respectively. Triangles represent samples from natural fermentation (NAT), while circles correspond to those from sivigliano fermentation (SIV). Different olive sizes are indicated by varying point diameters (G = 71–80 pieces/kg; M = 91–120 / 121–180 pieces/kg).

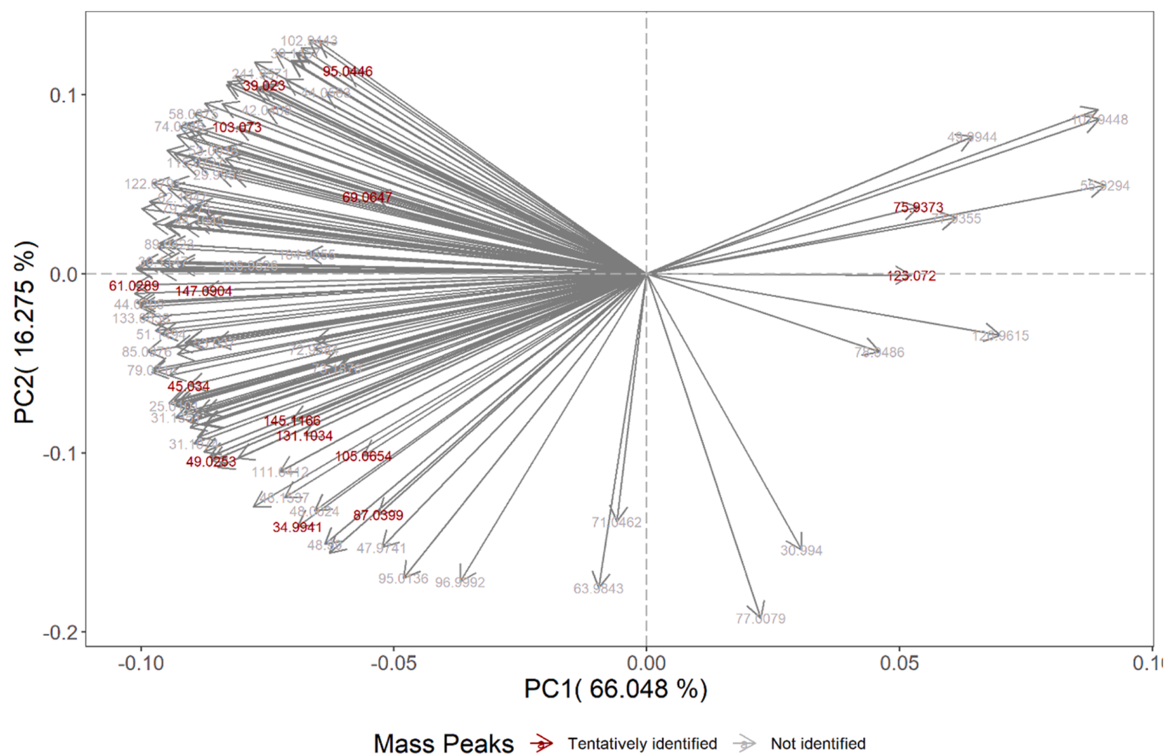

Fig. 2. Loading plot indicating the contribution of mass peaks to the observed separation in Fig. 1, with arrows representing individual VOCs. Mass peaks with tentatively identified also by GC-MS are red-coloured text.

fermentation method along the PC1 axis, indicating that fermentation mode is the principal factor driving variability. In contrast, olive size

had a negligible influence on the variance explained by either PC1 or PC2. Minimal differences were observed between SIV-fermented olives and their respective brines, whereas NAT-fermented samples showed clear differentiation between the olive matrix and the corresponding brine (Fig. 1). To better highlight the effect of fermentation, Table 2 reports the abundance of the detected mass peaks and their statistical differences (ANOVA, $p < 0.05$) grouped by fermentation process. The occurrence of multiple volatile compounds in Table 2 may reflect the presence of isomeric compounds in the PTR-ToF-MS data, potentially leading to overlapping ion signals. Compound identities were supported by complementary GC–MS analyses and verified through comparison with reference data in the literature (Table 2). To visualise the complex volatile fingerprints of the different matrices, a heatmap was generated (Fig. 3), offering a more intuitive representation, supporting the exploration of the numerical data. Hierarchical clustering was performed using Euclidean distance and the complete linkage method to group samples based on similarities in their volatile profiles. The accompanying dendrogram corroborates the groupings observed in the PCA. The heatmap includes only VOCs that were tentatively identified by GC-MS or through literature comparison. Two main clusters were clearly distinguished, corresponding to the different fermentation strategies. At the same time, the NAT samples were further divided into two subclusters, one corresponding to the olives and the other to their respective brines. In same cases, VOCs intensity was higher in brines. It could indicate a greater metabolic activity in the liquid phase or reflect physicochemical partition dynamics between the olive tissue and the respective aqueous medium [25]. During fermentation, volatile compounds produced within the fruit can diffuse into the brine and redistribute according to their polarity, solubility, and affinity for the liquid phase [32]. Furthermore, salt concentration and water activity may promote salting-out effects, enhancing VOC release into the headspace and consequently increasing their apparent signal intensity in PTR-ToF-MS analysis. This observation leads to an important consideration as the brine could be considered as a relevant source of aroma rather than as waste. It could serve for volatile recovery or for fermentation monitoring, focusing on specific VOC markers that are detected at low level in the fruit. Differently, this separation between olive fruits and brines in terms of volatilome was less evident in SIV samples. As illustrated in Fig. 3, the volatile profile of samples fermented using the NAT method exhibited greater chemical diversity, reflecting distinct microbial activity compared with the more standardised Spanish (SIV) fermentation. The NAT process relies solely on brine treatment (i.e. 10 % NaCl) for debittering, resulting in a slower and more spontaneous fermentation. This extended and less-controlled process enables the establishment of a complex microbial ecosystem, ultimately contributing to the development of a more intricate and often more nuanced sensory profile [33]. In contrast, the SIV protocol includes an additional alkali treatment (i.e. 2 % NaOH) before brining, which facilitates faster debittering but substantially reduces the native microbiota, yielding a less complex product in terms of VOCs [34]. As with other fermented products, it is well established in the literature that, during fermentation, microbial consortia evolve dynamically, with continuous interactions and competition among species resulting in significant shifts in metabolic activity [35,36]. These changes are reflected in the volatilome, which can serve as an indicator of the fermentation stage [16]. In general, the early stage of fermentation (approximately the first 30 days) is dominated by aldehydes; the intermediate stage (30–90 days) is characterised by the appearance of styrene and isoamyl alcohol; and the late stage (up to 180 days) by the accumulation of ethyl esters and fatty acids [37], the phase more near to the final products. The volatile compounds detected across the different matrices were classified into major chemical groups, including alcohols, aldehydes, ketones, esters, acids, aromatic hydrocarbons, sulfur compounds, and furans, as well as several molecular fragments and derivatives (Table 2).

The most representative volatile compounds identified as potential markers of fermentation were ethanol, acetaldehyde, acetic acid, propionic acid, and esters. These compounds are indicative of ongoing alcoholic and heterolactic fermentation (ethanol, acetic acid, acetaldehyde) or propionic fermentation (propionic acid), as previously reported by [38]. All were detected at higher concentrations in NAT samples (Fig. 3). Ethanol (*m/z* 47.050), also observed by [16] in another cultivar is associated with the fermentation process. Its production could involve bacteria or yeasts. In case of yeasts, ethanol production could be related to their metabolism and the Crabtree effect, whereby certain yeasts ferment glucose to ethanol even under aerobic conditions when glucose concentrations are high. Yeasts are therefore classified as either Crabtree-positive or Crabtree-negative depending on this metabolic trait [39]. The presence of ethanol in SIV samples, although at lower concentrations, is likely attributable to heterofermentative lactic acid bacteria (LAB), which, together with homofermentative LAB, are predominant or selectively favoured in Spanish-style fermentations [40]. LAB and yeasts, in fact, are the principal microbial groups driving table olive fermentation, both of which play essential roles in flavour development through the production of volatile compounds [41]. LAB can be classified as homofermentative or heterofermentative, depending on their metabolic pathways. Homofermentative LAB mainly produce lactic acid via the Embden–Meyerhof pathway, while heterofermentative LAB generate lactic acid together with ethanol, acetate, and CO_2 through the 6-phosphogluconate/phosphoketolase pathway [38]. Acetaldehyde (*m/z* 45.034) serves as a metabolic intermediate that is rapidly reduced to ethanol by alcohol dehydrogenase due to its reactive and unstable nature. Occasionally, acetaldehyde may accumulate, leading to undesirable flavour defects in the final product [42]. In the present study, ethanol concentrations exceeded those of acetaldehyde in both NAT and SIV samples, consistent with active reduction of acetaldehyde. Moreover, ethanol and acetaldehyde are also produced during the ripening process and considered as important precursor of natural aroma [20]. Acetic acid (*m/z* 61.029) was also more abundant in NAT samples, reflecting distinct microbial activity and metabolic pathways compared with SIV fermentations. This compound plays a central role in ester formation through reactions with ethanol [1]. Propionic acid (*m/z* 75.045) was detected across all samples, with the highest concentrations again found in NAT samples. Its presence suggests the activity of *Clostridium* or *Propionibacterium* spp., which are generally associated with propionic fermentation. The markedly lower abundance of this compound in SIV samples provides indirect evidence that the alkaline step in Spanish-style fermentation selectively suppresses spoilage-associated microorganisms, including those implicated in the so-called *zapatera* defects [43]. Propionic acid is produced via lactic acid degradation and may be further metabolised into a range of C_2–C_6 volatile acids during spoilage [44]. Among the ester compounds, ethyl acetate (*m/z* 89.060) emerged as the most significant volatile, serving as a marker of the late (third) fermentation stage [16,45]. Ethyl acetate is formed during heterolactic fermentation through the esterification of acetic acid with ethanol in the aqueous phase [46]. It is well established that acetate esters are synthesised by alcohol acyltransferases, which catalyse the reaction between volatile alcohols and acetyl-CoA to produce esters and CoA-SH [47]. Previous studies have consistently identified ethyl acetate as a key flavour compound in heterofermentative pathways [1,48]. The PTR-ToF-MS signal at *m/z* 89.060 may also include additional volatiles, such as 2-methylpropanoic acid, 3-hydroxy-2-butanone (acetoin), and butanoic acid, all of which were confirmed as distinct compounds by GC–MS analysis. Butanoic acid (butyric acid) is particularly noteworthy as a marker of butyric spoilage, imparting a rancid odour to the product [44]. Propyl acetate (*m/z* 103.073) was also detected, likely formed via the esterification of volatile alcohols with acetyl-CoA, and was more abundant in NAT samples. Interestingly, the *m/z* 75.045, tentatively identified as propionic acid, may also correspond to methyl acetate (the methyl ester of acetic acid), which was present at comparable levels. The brine samples (WM and WG) generally contained higher concentrations of these VOCs than the corresponding olive matrices, except for ethanol in NAT samples, where

Table 2
The main volatile organic compounds (VOCs) detected through PTR-ToF-MS in each sample were classified into two groups based on statistically significant differences determined by one-way ANOVA (p-value<0.05) and Fisher's post-hoc test. Letters were assigned based on the results of the Fisher's post hoc test, where different letters indicate statistically significant differences between groups (p-value<0.05). Where possible, mass peaks are assigned to protonated formulas with tentative identifications, flavour description.

			Concentration (ppbv)									
Measured mass	Theoretical mass	Protonated formula	Natural			Sivigliano			Tentative identification	Volatile marker	Flavor Profile	Ref.
34.994	34.9955	[H2S]H+	0.530	±	0.182a	0.156	±	0.054b	hydrogen sulfide	Microbial origin (sulfite-reducing bacteria)	Egg, rotten	[54]
45.034	45.0340	[C2H4O]H+	489,317.000	±	55799a	68,559.000	±	42074b	acetaldehyde	Alcoholic fermentation	Floral, Green Apple	[16]
47.050	47.0496	[C2H6O]H+	2420,314.000	±	625261a	158,510.000	±	43042b	ethanol	Alcoholic and/or heterolactic fermentation	Alcoholic, ethereal	[46]
57.070	57.0704	[C4H8]H+	70,809.000	±	66737a	15,124.000	±	8090b	1-butanol dehydrated form*	Alcoholic fermentation	Fruit	[1]
									2-butanol dehydrated form*	LAB activity	not found	[55]
61.029	61.0289	[C2H4O2]H+	2165,737.000	±	1639673a	127,124.000	±	46818b	acetic acid*	Alcoholic and/or heterolactic fermentation	Acid, Fruit, Pungent, Sour, Vinegar	[16]
63.023	63.0268	[C2H6S]H+	167,225.000	±	63254a	32,083.000	±	17085b	dimethyl sulfide	Yeast activity	Cabbage, Green, Sulfurous	[55]
69.034	69.0340	[C4H4O]H+	0.658	±	0.325a	0.162	±	0.045b	furan	Oxidation reaction	Ethereal	[1, 16]
71.082	71.0860	[C5H10]H+	6334.000	±	0.898a	0.918	±	0.249b	2-pentanol dehydrated form	LAB activity	Burnt, Cocoa, Floral, Malt	[56]
73.061	73.0653	[C4H8O]H+	53,449.000	±	57357a	1978.000	±	1690b	butanal	Bacterial metabolism	Banana, Green, Pungent	[38]
									2-butanone	Yeast activity	Fragrant, Fruit, Pleasant	[16, 38]
75.045	75.0440	[C3H6O2]H+	517,131.000	±	437071a	87,149.000	±	54919b	propionic acid*	*Clostriudium / Propionibactetium* acitvity	Fat, Fruit, Pungent, Silage, Soy	[55]
									acetic acid methyl ester*	LAB activity	Ester, Green	[55]
75.937	75.9441	[CS2]H+	0.018	±	0.013b	0.451	±	0.484a	carbon disulfide*	-	not found	
77.046	77.0714	[C2H8N2O]H+	2861.000	±	2291a	0.521	±	0.288b	2-hydrazinoethanol*	-	not found	
87.040	87.0446	[C4H6O2]H+	1508.000	±	0.735a	0.309	±	0.026b	2-methyl-2-propenoic acid	LAB activity	not found	[1]
87.077	87.0809	[C5H10O]H+	0.643	±	0.300a	0.271	±	0.056b	pentanal*	Lipoxygenase pathway / microbial activity	Almond, Bitter, Malt, Oil, Pungent	[57]
89.060	89.0602	[C4H8O2]H+	1342,529.000	±	1070712a	31,864.000	±	22927b	ethyl acetate*	Heterolactic fermentation/ third stage of fermentation	Aromatic, Brandy, Grape	[1]
									2-methyl-propanoic acid*	LAB activity	Burnt, Butter, Cheese, Sweat	[1]
									3-hydroxy-2-butanone*	Heterolactic fermentation	Butter, Creamy, Green Pepper	[58]
									butanoic acid*	Microbial spoilage	Butter, Cheese, Sour	[44]
91.063	91.0759	[C4H10O2]H+	10,326.000	±	7607a	0.254	±	0.148b	2,3-butanediol*	Heterolactic fermentation	Fruity, Creamy, Buttery	[54]
93.041	93.0551	[C3H8O3]H+	5332.000	±	1657a	2269.000	±	0.389b	glycerin*	Yeast activity	Sweet	[56]
93.085	93.0704	[C7H8]H+	58,979.000	±	19231a	0.093	±	0.097b	toluene	Ripening	Sweet	[16]
101.057	101.0602	[C5H8O2]H+	0.123	±	0.035a	0.056	±	0.004b	2,4-pentanedione	-	not found	
101.091	101.0966	[C6H12O]H+	0.060	±	0.020a	0.029	±	0.007b	3-hexen-1-ol*	Lipoxygenase pathway	Grass, Green Fruit, Green Leaf, Herb, Unripe Banana	[1]
									cyclohexanol*	Microbial activity	not found	[51]
103.073	103.0730	[C5H10O2]H+	27,873.000	±	33535a	0.476	±	0.265b	propyl acetate*	LAB activity	Celery, Floral, Pear, Red Fruit	[55]
									propionic acid ethyl ester (ethyl propanoate)*	Microbial activity / third stage of fermentation	Apple, Pineapple, Rum, Strawberry	[1]
105.065	105.0704	[C8H8]H+	0.819	±	0.380a	0.129	±	0.049b	styrene*	Third stage of fermentation	Sweet, Balsam, Floral, Plastic	[16]
109.072	109.0653	[C7H8O]H+	0.193	±	0.135a	0.021	±	0.004b	benzyl alcohol	Phenylalanine fermentation	Boiled Cherries, Moss, Roasted Bread, Rose	[1]
117.087	117.0915	[C6H12O2]H+	0.872	±	0.303a	0.073	±	0.021b	isobutyl acetate*	Microbial activity / third stage of fermentation	Apple, Banana, Floral, Herb	[59]
119.066	119.0708	[C5H10O3]H+	0.257	±	0.074a	0.081	±	0.031b	ethyl lactate*	LAB activity	Cheese, Floral, Fruit, Pungent, Rubber	[45]
121.081	121.0653	[C8H8O]H+	1430.000	±	0.941a	0.044	±	0.015b	acetophenone	Lipoxygenase pathway	Almonds, Flower, Meat, Must	[1, 60]
123.072	123.0809	[C8H10O]H+	0.150	±	0.042b	0.269	±	0.121a	phenyl ethyl alcohol*	LAB activity	Fruit, Honey, Lilac, Rose, Wine	[45]

(*continued on next page*)

Table 2 (*continued*)

Measured mass	Theoretical mass	Protonated formula	Concentration (ppbv) Natural		Sivigliano		Tentative identification	Volatile marker	Flavor Profile	Ref.
125.054	125.0602	$[C_7H_8O_2]H^+$	0.080	± 0.037a	0.018	± 0.003b	4-ethyl phenol *	LAB activity	Leather, Phenol, Spice, Stable	[1]
							2-methoxy phenol *	Third stage of fermentation	Burnt, Phenol, Wood	[56]
127.073	127.1122	$[C_8H_{14}O]H^+$	0.240	± 0.274a	0.016	± 0.004b	1-octyn-4-ol*	Microbial activity	not found	[57]
							6-methyl-5-hepten-2-one *	LAB activity	Citrus, Mushroom, Pepper, Rubber, Strawberry	[1]
129.088	129.0915	$[C_7H_{12}O_2]H^+$	0.384	± 0.429a	0.028	± 0.004b	cyclohexanoic acid	Zapatera spoilage	Fruit	[55]
131.103	131.1072	$[C_7H_{14}O_2]H^+$	0.340	± 0.126a	0.022	± 0.008b	1-butanol 3-methyl acetate (isopentyl acetate)*	Yeast activity	Apple, Banana, Pear	[55]
							6-hepten-2,4-diol*	-	not found	
							butanoic acid 3-methyl ethyl ester (Ethyl isovalerate)*	Third stage of fermentation	Apple, Fruit, Pineapple, Sour	[16]
							2-methyl-hexanoic acid *	-	Dairy	
139.070	139.0759	$[C_8H_{10}O_2]H^+$	0.033	± 0.003a	0.018	± 0.002b	2-methoxy-5-methyl phenol*	Ripening	not found	[61]
145.117	145.1228	$[C_8H_{16}O_2]H^+$	0.043	± 0.010a	0.012	± 0.001b	hexanoic acid ethyl ester (Ethyl hexanoate)*	Third stage of fermentation	Apple Peel, Brandy, Fruit Gum, Overripe Fruit, Pineapple	[16]
147.090	147.1021	$[C_7H_{14}O_3]H^+$	0.024	± 0.018a	0.002	± 0.001b	butanoic acid, 2-hydroxy-3-methyl-, ethyl ester	Third stage of fermentation	Pineapple, Strawberry, Tea, Honey	[16]
151.082	151.0759	$[C_9H_{10}O_2]H^+$	0.016	± 0.005a	0.005	± 0.001b	acetic acid, phenylmethyl ester	Third stage of fermentation	Fruit	[16]
163.093	163.0759	$[C_{10}H_{10}O_2]H^+$	0.759	± 0.813a	0.007	± 0.003b	safrol / isosafrol	Plant-derived	Sweet, Warm, Spicy Woody, Floral, Sassafras, Anise	[16]

* VOCs also detected by SPME-GC–MS.

slightly lower levels were observed. The elevated abundance of ethyl acetate in brines is consistent with its formation through the esterification of acetic acid and ethanol in the aqueous phase. Similar findings were reported by [16], who detected ethanol, acetaldehyde, and ethyl acetate by PTR-ToF-MS in a different olive cultivar. Among these, acetic acid, propionic acid, ethyl acetate, and propyl acetate were also confirmed by GC–MS in the present study (Table 2). These results align closely with previous GC–MS-based investigations: for example, De Angelis et al. [1] identified ethanol and ethyl acetate in *cv. Bella di Cerignola*, while Sabatini et al. [46] detected both compounds in olives and brines from another cultivar. Other compounds found at higher concentrations in NAT samples, and that may serve as indicators of fruit maturity, include toluene (m/z 93.085), typically associated with ripe fruits [16]. The low abundance of aldehydes, usually dominant in the early stages of maturation, further confirms the advanced ripening status of the olives analysed [49].

Among the VOCs detected at lower concentrations but still relevant as indicators of specific metabolic pathways, alcohols deserve particular attention (Table 2). These compounds were consistently present at low levels across all samples. They are typically released through the activation of the lipoxygenase (LOX) pathway, which is initiated following cell disruption, such as cutting or mechanical stress. This enzymatic activity leads to the formation of several C_5 and C_6 volatiles, which are also produced during malaxation and contribute to the characteristic aroma of olive oil [50]. In the present study, the occurrence of specific volatiles suggests that a lipoxygenase-like metabolism of polyunsaturated fatty acids may also occur in fermented olives. This process could be triggered by enzymes released into the brine by lactic acid bacteria, yeasts, or other microorganisms. The detection of 3-hexen-1-ol (m/z 101.091) supports the activation of the LOX pathway. Cyclohexanol, detected at the same m/z and identified as a distinct compound by GC–MS, has not been previously reported in table olives or olive oil. Its presence likely reflects microbial activity, as suggested by [51]. Both compounds were detected in all samples, with the highest concentrations found in NAT brines (WM, WG) [1]. Another notable alcohol, detected at high levels in SIV samples, was phenylethyl alcohol (m/z 123.072), an aromatic compound with a floral, rose-like note, commonly found in fermented foods and essential oils. Its presence is typically linked to yeast metabolism, particularly *Saccharomyces cerevisiae*, which converts L-phenylalanine to phenylethyl alcohol via the Ehrlich pathway [52]. Another compound detected at the same m/z value in PTR-ToF-MS and confirmed independently by GC–MS was 4-ethylphenol, which imparts negative aromatic notes and may be produced during lactic acid fermentation in a strain-dependent manner [53].

The investigation of the volatile metabolome, unlike other metabolomic approaches, enables the rapid acquisition of critical information related to fermentation conditions and the biochemical characteristics of the final product. It also allows for quick assessment of the fermentation stage and fruit ripening status. In this context, PTR-ToF-MS, owing to its exceptional speed and sensitivity, represents a powerful analytical tool. When combined with HS-SPME-GC–MS, the gold standard for compound separation and definitive identification, the analytical workflow becomes both rapid and comprehensive, allowing for high-resolution characterisation of complex fermentation processes. Although this study examines the volatilome at a single time point, the findings suggest strong potential for monitoring how VOCs change over time, which will be addressed in future research to better understand their evolution during fermentation.

4. Conclusion

This work presents the first integrated PTR-ToF-MS and GC–MS volatilomic analysis of cv. *Bella di Cerignola* table olives and their brines, offering new insights into the microbial and metabolic processes underpinning two traditional fermentation styles. NAT fermentation

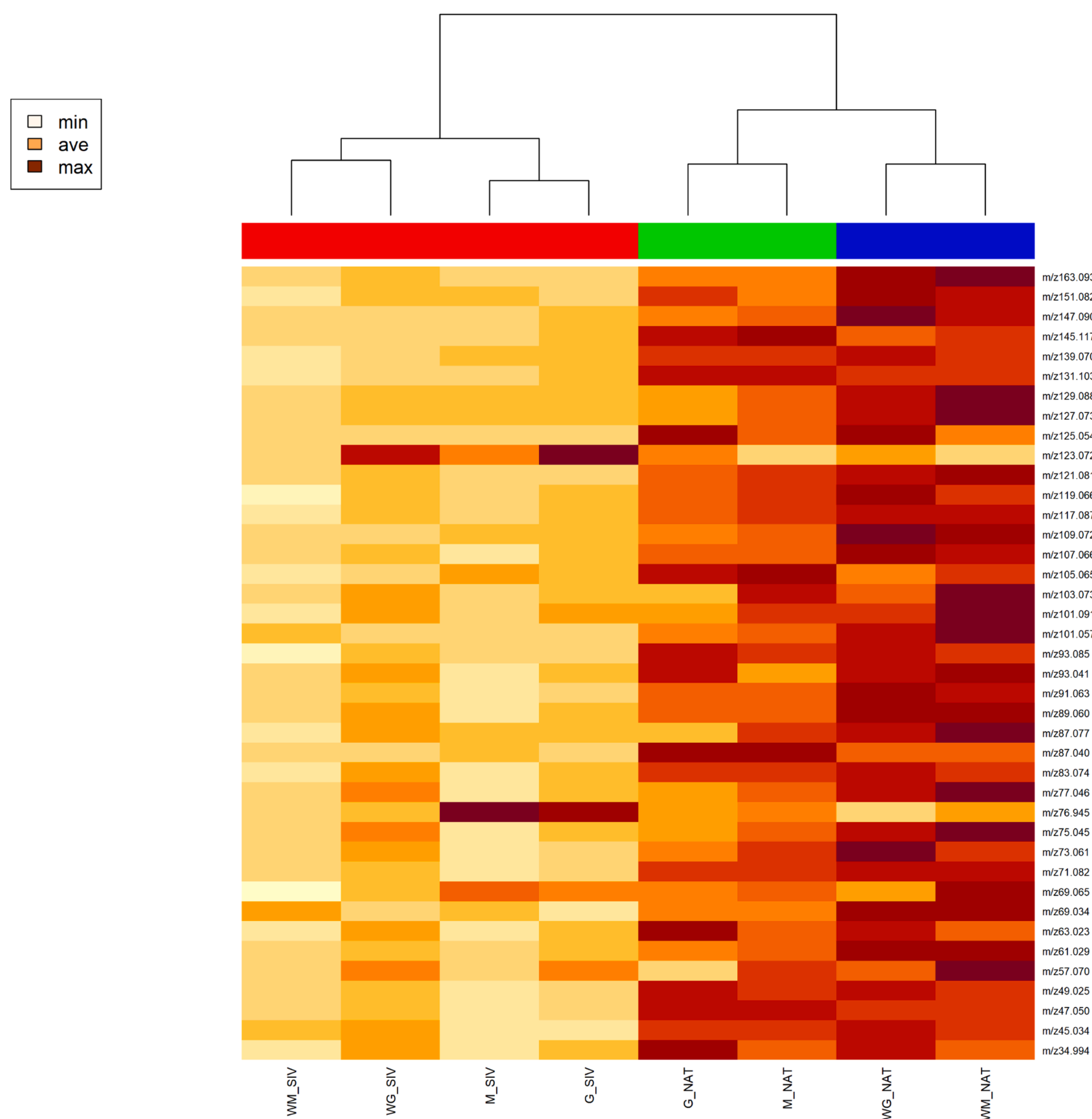

Fig. 3. Heatmap of volatile organic compounds detected in table olive and brine samples, based on PTR-ToF-MS analysis. Each column represents a sample, while each row corresponds to a specific volatile compound. The colour gradient indicates the relative abundance of each compound (from minimum to maximum, as shown in the legend). Samples are grouped by hierarchical clustering (top dendrogram), revealing clear differences between fermentation methods and olive sizes. Notably, Sivigliano samples (SIV) cluster separately from natural fermentation samples (NAT), reflecting distinct volatile profiles.

exhibited a substantially more complex and diverse volatile profile than the SIV process, revealing the influence of spontaneous microbial succession on product aroma and biochemical richness. The NAT volatilome was dominated by ethanol, acetic acid, acetaldehyde, propionic acid, and ethyl esters, compounds linked to yeast and hetero-fermentative lactic acid bacteria activity. In contrast, the SIV process, constrained by alkaline pretreatment, produced a more homogeneous profile. The detection of secondary alcohols, such as 3-hexen-1-ol and phenylethyl alcohol, further indicated the activation of lipoxygenase-like and yeast-associated metabolic routes.

The study demonstrates that PTR-ToF-MS provides rapid assessment of VOCs during fermentation, which is particularly useful for comparing fermentation styles and identifying key volatile markers. When complemented by GC–MS for structural identification, the integrated workflow achieves both analytical speed and interpretive depth. Beyond analytical innovation, the results contribute to a better understanding of the relationship between microbial ecology, metabolite diversity, and product quality in fermented vegetables. The approach proposed here can serve as a framework for the development of precision monitoring strategies, the selection of targeted starter cultures, particularly when combined with metataxonomic data, and the valorisation of artisanal fermentation practices in the table olive industry.

CRediT authorship contribution statement

Antonia Corvino: Writing – original draft, Software, Methodology, Formal analysis, Data curation, Conceptualization. **Iuliia Khomenko:** Writing – review & editing, Software, Methodology, Formal analysis, Data curation. **Emanuela Betta:** Software, Methodology, Investigation, Data curation. **Vittorio Capozzi:** Writing – review & editing, Visualization, Supervision, Project administration, Methodology, Conceptualization. **Franco Biasioli:** Writing – review & editing, Visualization, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.meafoo.2026.100287.

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