



Taste it, enjoy it. it's olive oil.

| 24

MADRID, SPAIN
26-28 JUNE 2024

**Spanish National
Research Council (CSIC)**



Organiza:



Colaboradores institucionales:



CSIC
CONSEJO NACIONAL DE INVESTIGACIONES CIENTÍFICAS



ICEX

#alimentosdespaña

**EL PAÍS
MÁS RICO DEL
MUNDO**



MINISTERIO DE AGRICULTURA, PESCA Y ALIMENTACIÓN

VIRGIN OLIVE OIL VOLATILE COMPOUNDS AND THEIR SENSORY PROPERTIES

DR. SC. KAROLINA BRKIĆ BUBOLA
INSTITUTE OF AGRICULTURE AND TOURISM, POREČ, CROATIA



MADRID, JUNE 27TH, 2024

VOO VOLATILE COMPOUNDS

- The aroma of VOO is one of the most important properties of this product and plays a major role in consumer choice.
- The VOO aroma is attributed to **the volatile compounds formed during and after the extraction of the oil from the olive fruits.**
- **More than 180 volatiles** have been identified in the VOO (Genovese et al., 2021)
- The VOO aroma is a complex mixture of volatile compounds, which includes **aldehydes, alcohols, ketones, hydrocarbons, esters, terpenes, furans and volatile phenols.**



■ SENSORY CONTRIBUTION OF VOLATILES

VOLATILE COMPOUND	ODOUR THRESHOLD VALUE (mg/kg)	SENSORY PROPERTIES
HEXANAL	0.075	green apple, green grass
E-2-PENTENAL	0.3	green apple, tomato, pungent
E-2-HEXENAL	0.424	bitter almond, green fruit, bitter, astrigent
Z-2-PENTEN-1-OL	0.25	banana
HEXANOL	0.4	fruity, aromatic, alcoholic, rough
E-3-HEXEN-1-OL	1	green
Z-3-HEXEN-1-OL	1.1	green, banana, fresh, green grass
E-2-HEXEN-1-OL	5	green grass, green leaf, fruity, bitter, astrigent
HEXYL ACETAT	1.04	sweet, green, fruity, apple
PENTAN-3-ON	70	sweet, fruity
1-PENTEN-3-ON	0.0007	pungent, mustard

ODOUR ACTIVITY VALUE (OAV) = CONCENTRATION OF VOLATILE COMPOUND / ODOUR TRESHOLD VALUE; > 1 (DIRECT CONTRIBUTION); < SINERGISTIC CONTRIBUTION

FORMATION OF THE VOLATILES IN VOOs

VOO volatiles - formed during the oxidation of fatty acids.

Endogenous plant enzymes participating in the LOX pathway are responsible for the formation of volatiles associated with **the positive odour**, while **chemical oxidation and exogenous microorganism enzymes** are associated with the formation of volatiles that cause **negative odour properties**.

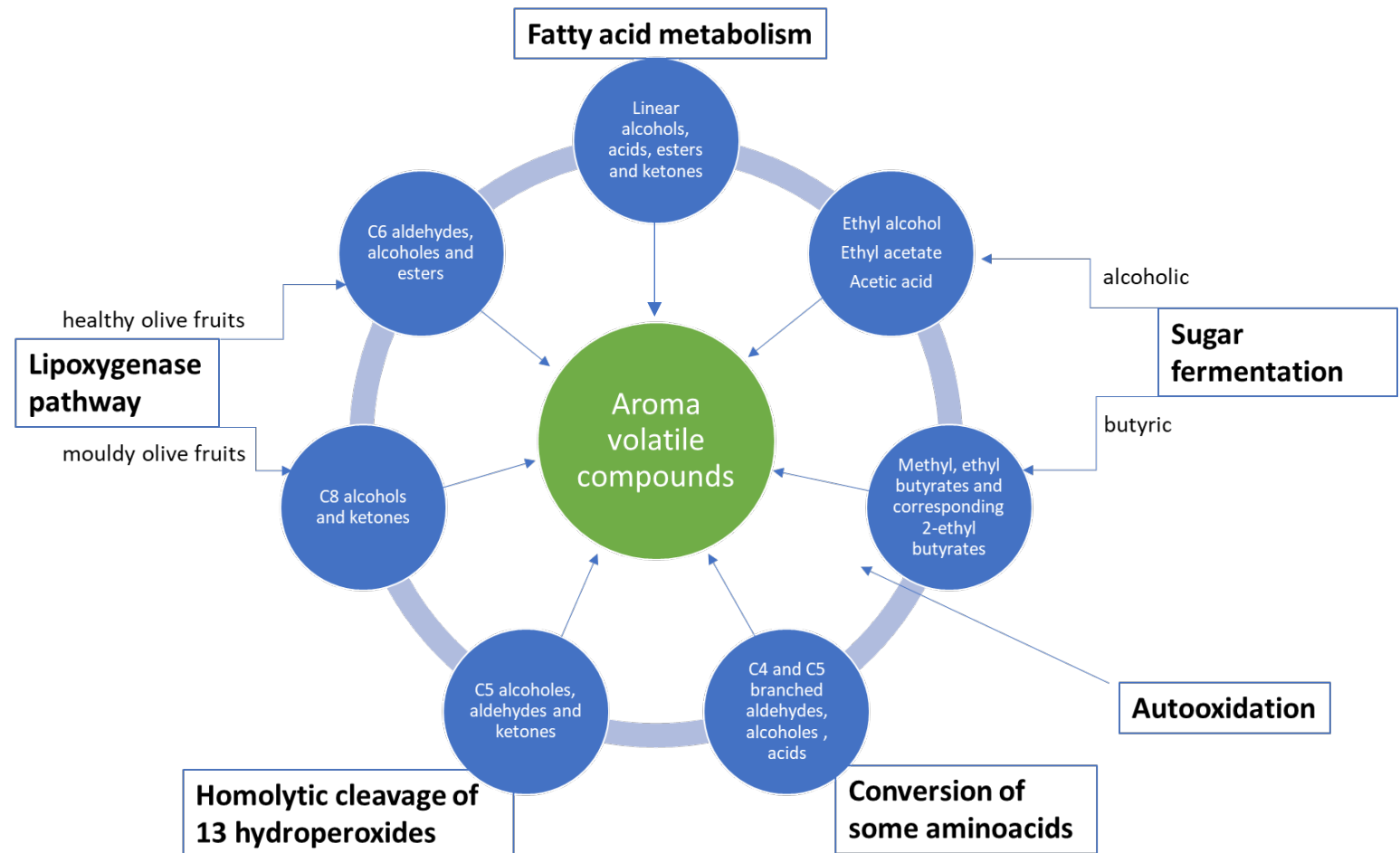
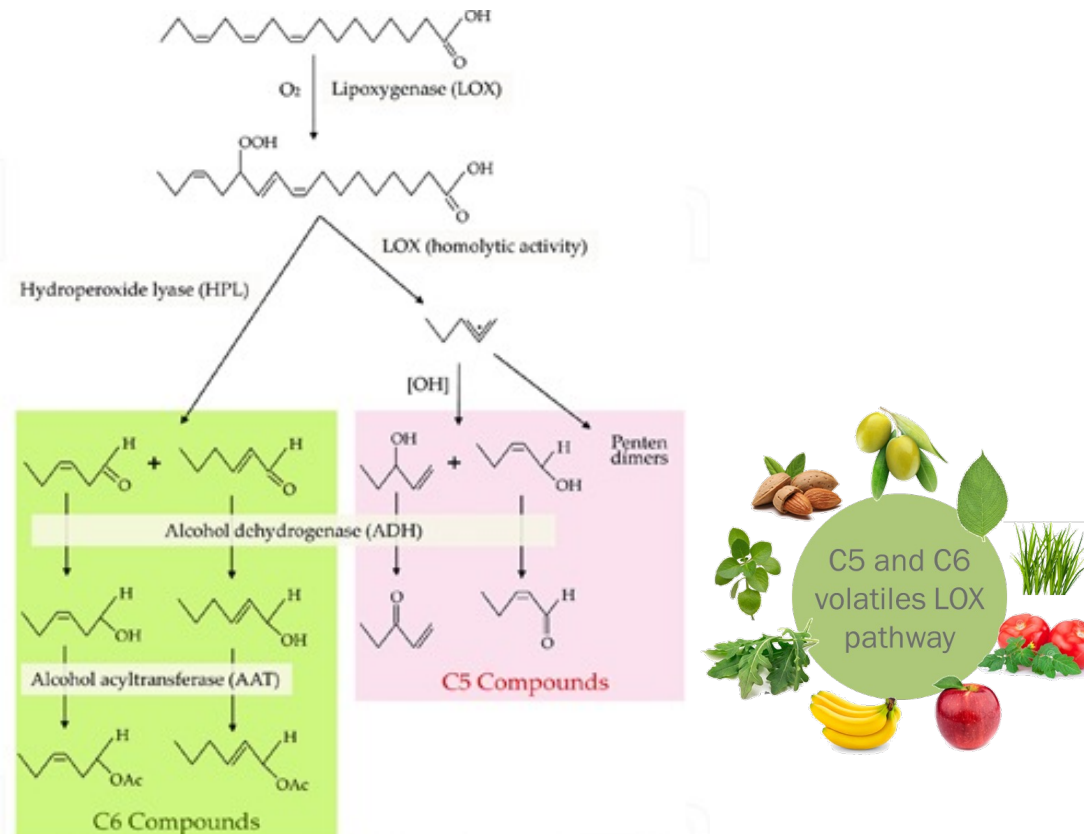


Fig. The main pathways involved in the formation of the volatile profile of virgin olive oils. Adapted from Angerosa et al. 2004; Angerosa 2002; Gomes da Silva et al., 2012.

POSITIVE ODOUR PROPERTIES



The **lipoxygenase pathway** is initiated by the release of enzymes when olive fruit tissues are disrupted.

The reaction pathway involves a series of enzymes that oxidise (lipoxygenase) and cleave (hydroperoxide lyase) polyunsaturated fatty acids to yield aldehydes.

These are subsequently reduced to alcohols (by alcohol dehydrogenase) and esterified to produce esters (by alcohol acyltransferase).

Fig. Lipoxygenase pathway for the formation of major volatiles (Benincasa et al., 2003; Gomes da Silva et al., 2012).

TYPE OF FRUITINESS

Fruity - Set of olfactory sensations characteristic of the oil which depends on the variety and comes from sound, fresh olives, either ripe or unripe (COI/T.20/Doc. No 15/Rev. 10).

- **Ripe fruitiness** – was associate to a high abundance of 3-hexanal, 2-hexanal and 2-hexenol – more C6 volatiles
- **Green fruitiness** – higher concentration of 2-pentanal and 1-penten-3-ol – more C5 volatiles
- **Green with ripe notes** – predominance of 1-penten-3-on, hexanal and hexanol

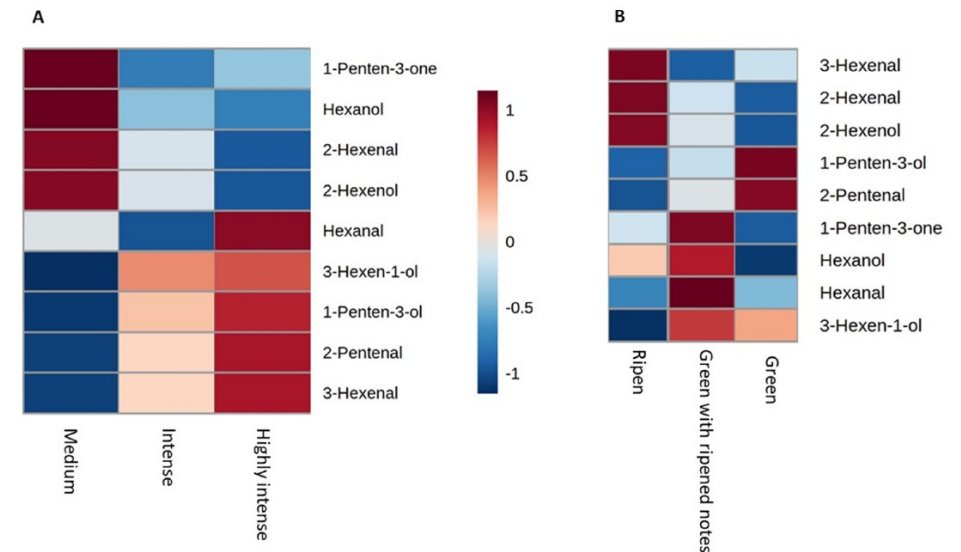


Fig. 3. Heatmap showing trends in relative concentration of LOX derived volatiles for (A) intensity and (B) type of fruitiness.

Source: Tomé-Rodríguez et al., Journal of Food Composition and Analysis, 2022.

■ NEGATIVE ODOUR PROPERTIES

NEGATIVE SENSORY ATTRIBUTES (DEFECTS)	DESCRIPTION (IOC, COI/T.20/DOC. NO 15/REV. 10 2018)	VOLATILES
Musty/humid/earthy	Characteristic flavor of oils obtained from fruit in which large numbers of fungi and yeasts have developed as a result of its being stored in humid conditions for several days or of oil obtained from olives that have been collected with earth or mud on them and which have not been washed.	C8 volatiles (oct-1-en-3-ol and oct-1-en-3-one) short chain fatty acids (Morales et al., 2005)
Fusty / Muddy sediment	Characteristic flavor of oil obtained from olives piled or stored in such conditions as to have undergone an advanced stage of anaerobic fermentation. Characteristic flavor of oil which has been left in contact with the sediment that settles in underground tanks and vats and which has also undergone a process of anaerobic fermentation.	The presence of ethyl butanoate, propanoic and butanoic acids (Morales et al., 2005)
Winey-vinegary	Characteristic flavor of certain oils reminiscent of wine or vinegar. This flavor is mainly due to a process of aerobic fermentation in the olives or in olive paste left on pressing mats which have not been properly cleaned and leads to the formation of acetic acid, ethyl acetate and ethanol.	The presence of acetic acid, ethanol, 3-methylbutan-1-ol and ethyl acetate (Morales et al., 2005)
Rancid	Flavor of oils which have undergone an intense process of oxidation.	The absence of C6 volatiles and the presence of several aldehydes with low odour thresholds (Morales et al., 2005)

GRUBBY DEFECT

Flavor of oil obtained from olives which have been heavily attacked by the grubs of the olive fly.



Article

Exploring the Connection between the Occurrence and Intensity of "Grubby" Defect and Volatile Composition of Olive Oil

Karolina Brkić Bubola ^{1,*}, Igor Lukić ¹, Marin Krapac ¹ and Olivera Koprivnjak ²

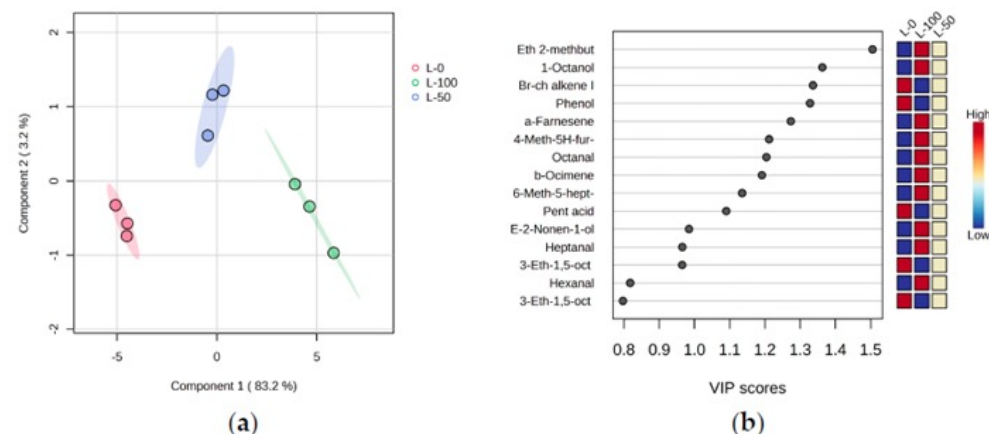
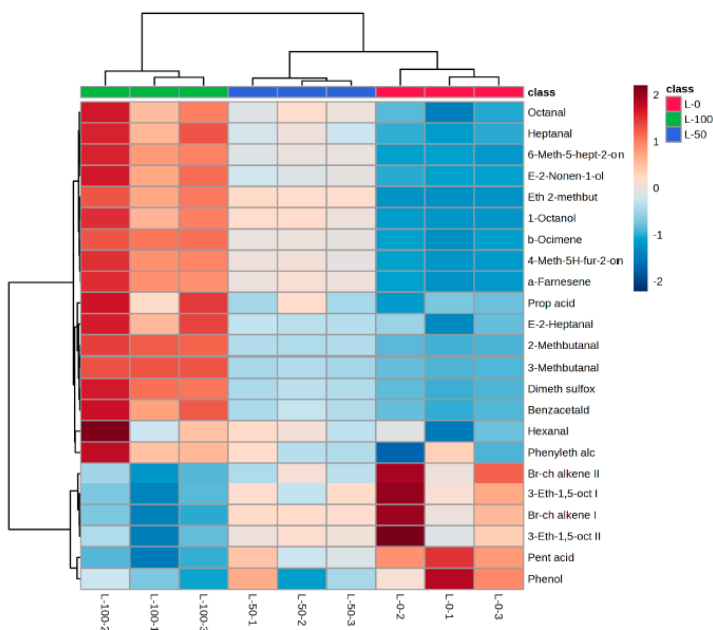


Figure 3. (a) Separation of virgin olive oils from fruits of the Leccino (L) cultivar with different levels of olive fly infestation (L-0: 0% infestation; L-50: 50% infestation; L-100: 100% infestation) in two-dimensional space according to partial least squares discriminant analysis (PLS-DA); (b) variable importance in projection (VIP) scores of selected volatile compounds as variables most useful for the separation.

Grubby defect - **3-methylbutanal**, **2-methylbutanal**, β -ocimene, ethyl 2-methylbutyrate, dimethyl sulfoxide, 4-methyl-5H-furan-2-one, α -farnesene, 6-methyl-5-hepten-2-one, 1-octanol, E-2-nonen-1-ol, benzeneacetaldehyde, heptanal, and octanal (Brkić Bubola et al., 2022).

FROSTBITTEN OLIVES

Characteristic flavor of oils extracted from olives which have been injured by frost while on the tree.

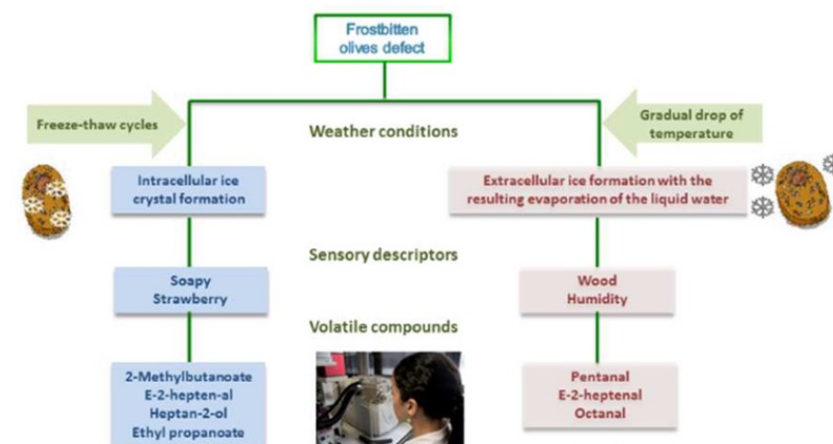
Existence of two sensory profiles of the 'frostbitten olives' defect:

- One characterized by **'soapy' and 'strawberry-like'** perceptions and the presence of **ethyl 2-methyl butanoate and ethyl propanoate**.
- The second characterized by **'wood' and 'humidity'** descriptors and a high concentration of **pentanal and octanal** (Romero et al., 2017).

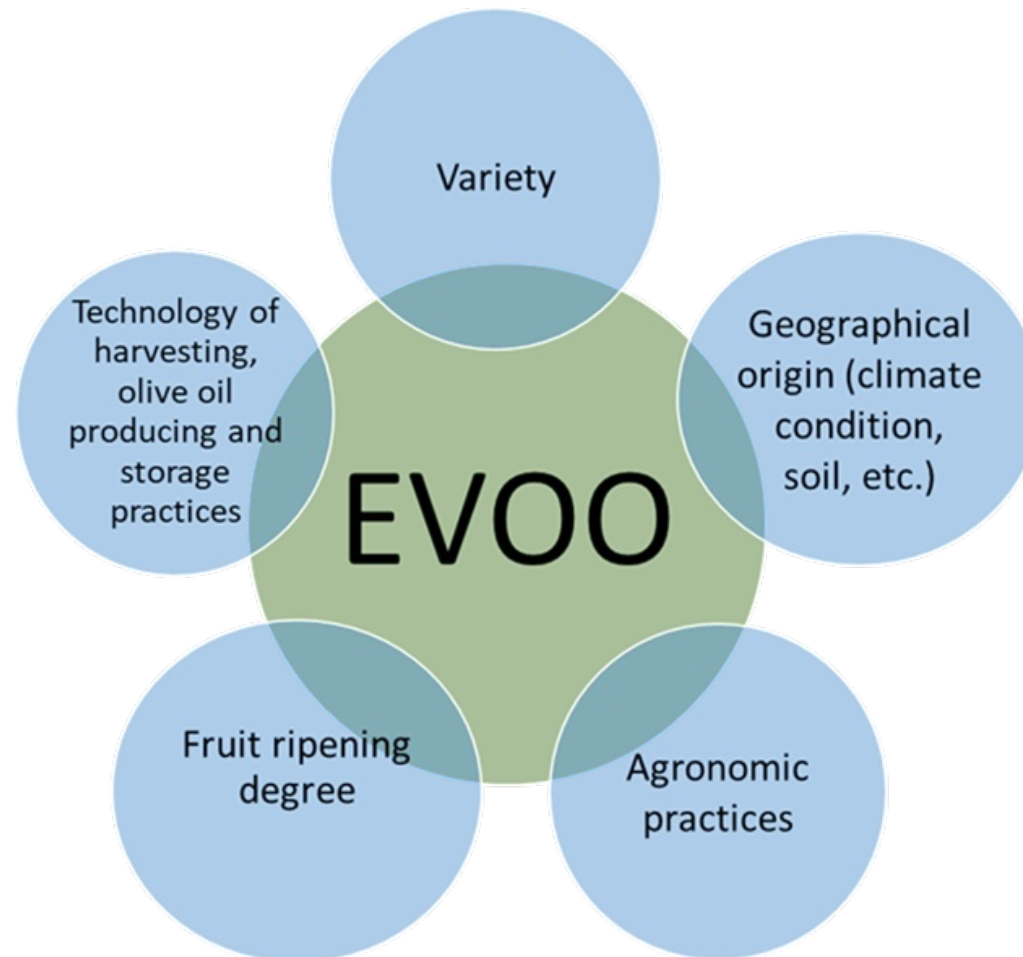
> J Agric Food Chem. 2017 May 31;65(21):4314-4320. doi: 10.1021/acs.jafc.7b00712.
Epub 2017 May 18.

Study of Volatile Compounds of Virgin Olive Oils with 'Frostbitten Olives' Sensory Defect

Inmaculada Romero ¹, Diego L García-González ¹, Ramón Aparicio-Ruiz ¹, María T Morales ²



FACTORS INFLUENCING VOO VOLATILES



■ SENSORY ANALYSIS

- **Sensory analysis** is an analytical procedure that uses people's senses as detectors. It is the most effective way to identify VOO sensory properties because **provides complete information about odor and taste and takes into account the interaction of taste and odor compounds**.
- **Panel test** is the official approach for **classification of VOO according to their organoleptic characteristics**, accived by a group of testers trained according to IOC standards.
- Although a complete description of the sensory characteristics of VOO can be obtained only by sensory analysis, the analytical methods for of volatile compounds determination can provide useful information about the quality of the product.



ANALYTICAL APPROACHES FOR VOO VOLATILES DETERMINATION

Several analytical approaches for VOO volatiles determination were developed. The most widely used and the most promising methods in terms of supporting sensory analysis:

JOURNAL OF
**AGRICULTURAL AND
FOOD CHEMISTRY**

pubs.acs.org/JAFC

Review

Virgin Olive Oil Volatile Compounds: Composition, Sensory Characteristics, Analytical Approaches, Quality Control, and Authentication

Lorenzo Cecchi, Marzia Migliorini, and Nadia Mulinacci*



Cite This: *J. Agric. Food Chem.* 2021, 69, 2013–2040



Read Online

HS-SPME-GC-MS is the most suitable technique to propose as a basis for developing a harmonized method widely applicable in testing laboratories (Cecchi et al., 2021).

SAMPLE PREPARATION METHODS

VOO complex matrix – wide chemical diversity, wide range of concentration.

The **head space solid phase micro extraction (HS-SPME)** from 1990 – the main advantages:

- There is no sample manipulation
- Easy and clean extraction method in just one step
- More fibers available – the most effective for extraction of compounds with low molecular weight – DVB/CAR/PDMS (divinylbenzene/carboxene/polydimethylsiloxane)
- Time and temperature of extraction important since affects equilibrium and extraction efficiency.

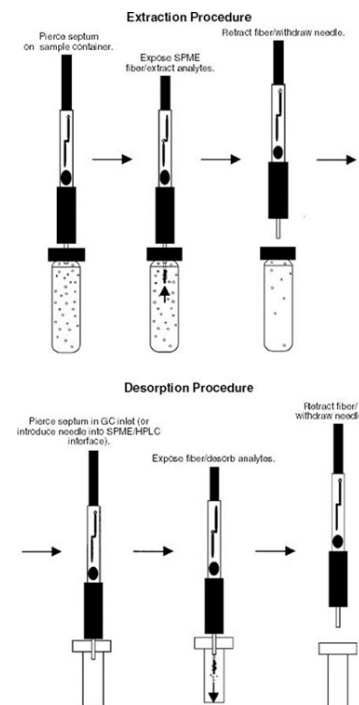


Fig. Ormsby, JAIC, 2005, 44,1, 2, 13-26.

■ CHROMATOGRAPHIC METHODS FOR OLIVE OIL VOLATILES ANALYSIS

- **Capillary gas chromatography (GC)** is the most used techniques for the separation of volatile compounds in olive oils.
- **The most common detector** used is **the flame ionization detector (FID)** due to its sensitivity and wide linear dynamic range.
- Coupled with **mass spectrometry (GC/MS)** **tentative identification** of volatile compounds can be achieved. Commercial spectral libraries are becoming more complete and specific, making GC/MS one of the most used techniques for routine identifications (Gomez da Silva et al., 2012)



ANALYTICAL SUPPORT OF SENSORY ANALYSIS

OLEUM METHOD FOR VOLATILE DETERMINATION – quality control, limits and ranges for volatiles in VOO of different origin and quality (20 laboratories involved, method using FID detector provide better results in terms of reproducibility than method using MS)

Received: 18 April 2023 | Revised: 12 September 2023

DOI: 10.1002/ejlt.202300079

European Journal of
Lipid Science and Technology

RESEARCH ARTICLE

Multianalyte analysis of volatile compounds in virgin olive oils using SPME-GC with FID or MS detection: results of an international interlaboratory validation

Diego L. García-González¹ | Enrico Casadei² | Ramón Aparicio-Ruiz^{1,3} | Clemente Ortiz Romero¹ | Enrico Valli² | Paul Brereton⁴ | Anastasios Koidis⁴ | Martyna Korytkowska⁴ | Maurizio Servili⁵ | Roberto Selvaggini⁵ | Florence Lacoste⁶ | Julien Escobessa⁶ | Stefania Vichi⁷ | Beatriz Quintanilla-Casas⁷ | Alba Tres⁷ | Pierre-Alain Golay⁸ | Paolo Lucci⁹ | Erica Moret¹⁰ | Alessandra Bendini² | Tullia Gallina Toschi²

The 18 volatile compounds quantified

(minimum number of highly diagnostic sensory markers)

Negative attributes (defects)

Fusty/muddy sediment (Total: 5)
Octane
Ethanol
3-methyl-1-butanol
Propanoic acid
6-methyl-5-hepten-2-one

Winey-vinegary (Total: 3)
Acetic acid
Ethyl acetate
Ethanol

Musty-humid-earthy (Total: 3)
(E)-2-heptenal
1-octen-3-ol
Propanoic acid

Frostbitten olives (wet wood) (Total: 1)
Ethyl propanoate

Rancid (Total: 5)
Hexanal
Nonanal
(E,E)-2,4-hexadienal
(E)-2-decenal
Pentanoic acid

Positive attribute (fruity)

Fruity (green notes) (Total: 3)
(E)-2-hexenal
(Z)-3-hexenyl acetate
1-hexanol



DETERMINATION OF VOLATILES IN VOO BY SPME GC-FID/MS

- Method of the determination of the content of selected volatile compounds in the headspace of VOO, responsible for the VOO aroma – OLEUM and IOC
- based on the extraction of volatile compounds by SPME and separation of the analytes by GC and quantification with a flame ionization detector (FID) or mass spectrometry (MS).

Descriptor	Volatiles
fusty-muddy sediment defect	octane, ethanol, 3-methyl-1-butanol, propanoic acid, 6-methyl-5-hepten-2-one
winey-vinegary defect	acetic acid, ethyl acetate, ethanol
musty-humid-earthly defect	(E)-2-heptenal, 1-octen-3-ol, propanoic acid
frostbitten olives defect	ethyl propanoate
rancid defect	hexanal, nonanal, (E,E)-2,4-hexadienal, (E)-2-decenal, pentanoic acid
fruity attribute	(E)-2-hexenal, (Z)-3-hexenyl acetate, 1-hexanol



*Taste it, enjoy it.
it's olive oil.*

Thank you for your attention!

E-mail: karolina@iptpo.hr