

# **5. La biogenesi delle note aromatiche negli oli extravergini**

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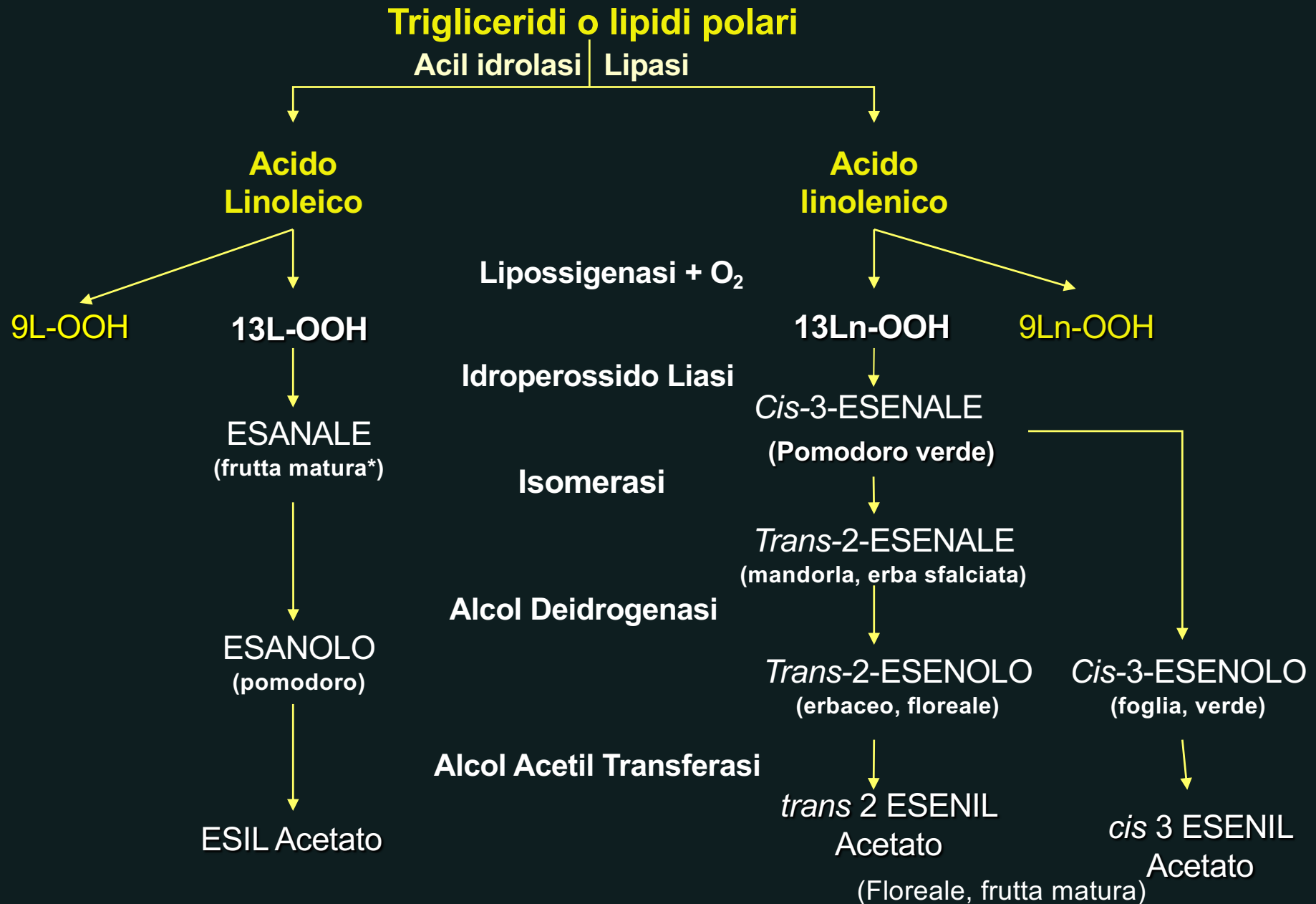


“Ogni oliva è un microcosmo, il risultato di un profondo equilibrio tra la pianta e il clima, il suolo, gli insetti, gli uccelli e l’uomo (che ne dovranno diffondere il seme, assicurando così la diffusione della specie).

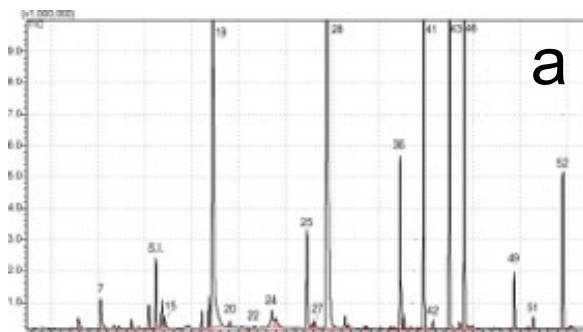
I profumi caratteristici delle diverse varietà di olivo sono il frutto di **complesse alchimie naturali** che determinano il prevalere di una reazione sull’altra e la genesi di alcuni composti e non di altri.”

R.Sacchi , M L. Ambrosino (2004) L’Olio extravergine di oliva: un “succo divino”, Relazione presentata al convegno “*Il mare delle diversità: specie, culture, prodotti*”, 10 dicembre.

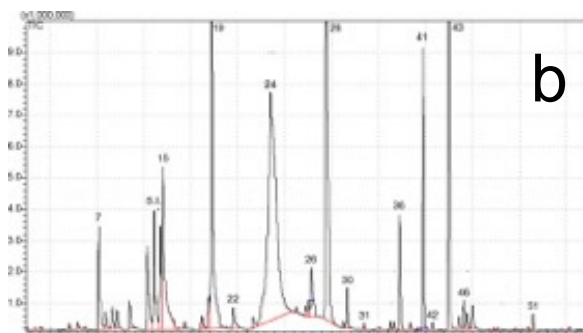
# Via delle Lipossigenasi (LOX-pathway)



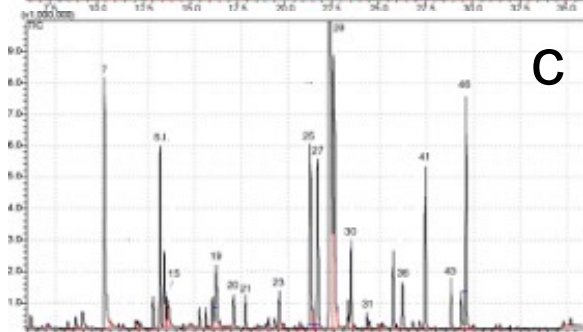




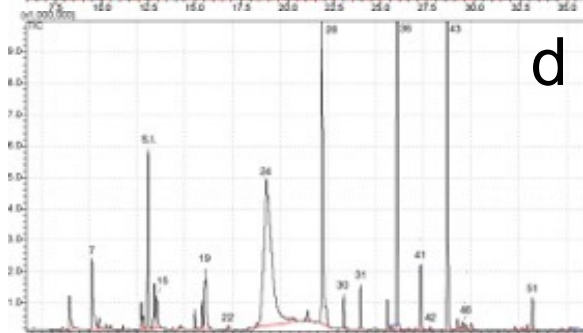
a



b



c



d

SPME GC/MS chromatogram of the headspace of some oils:

- a) PDO Bruzio (basilico),
- b) Cv Biancolilla (pomodoro),
- c) PDO Penisola Sorrentina, Minucciola (rosmarino),
- d) PDO Irpinia, cv.Ravece (pomodoro).

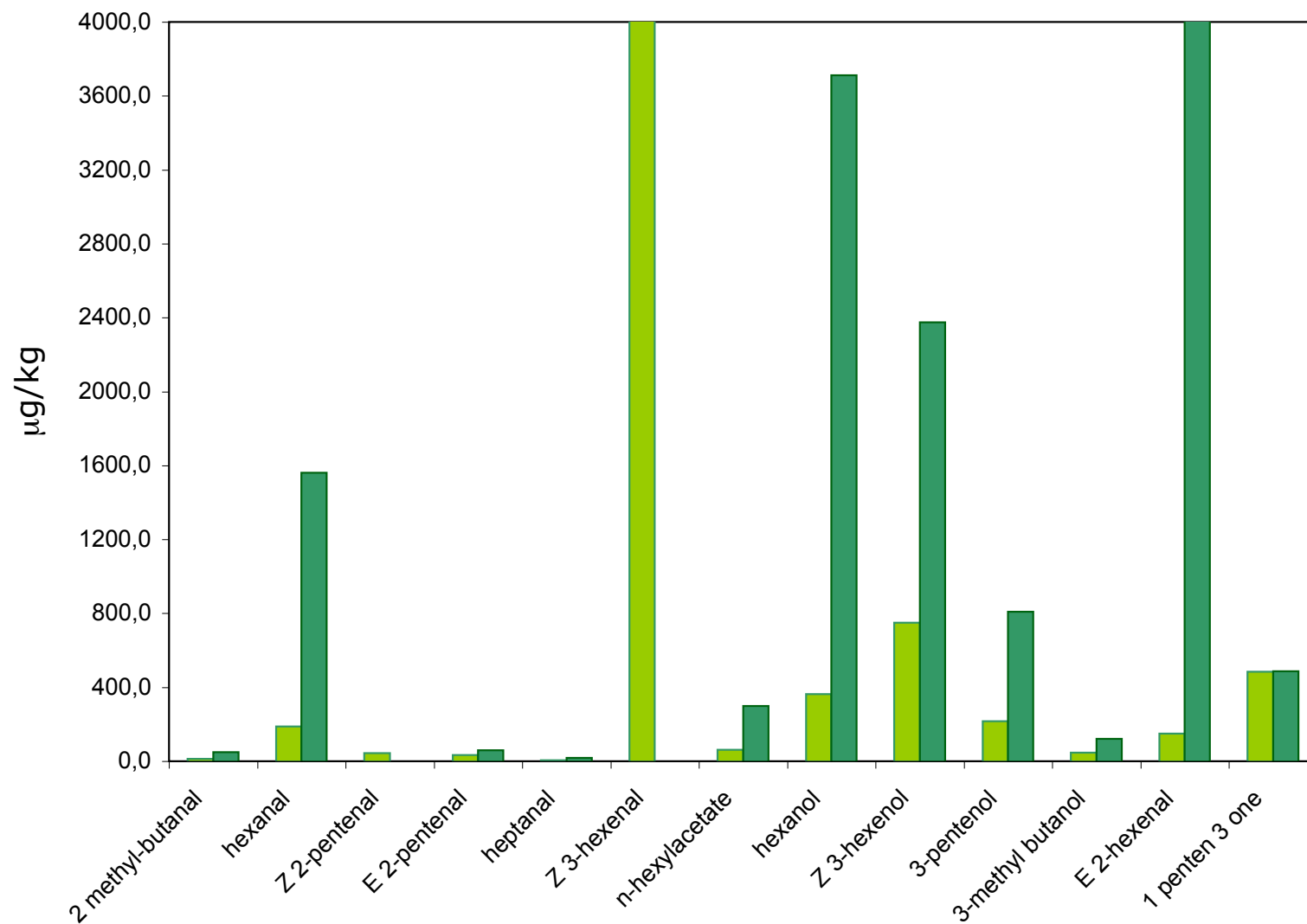
Peak identification of the main volatile compounds:

7. ethanol, 15. 3 pentenone, 19. hexanal, 20. pinene, 21. beta.-Phellandrene, 22. trans 2 pentenale, 23. beta.-Myrcene, **24. cis-3-Hexenal**, **25. D-limonene**, 26. 3 methyl butanol, **27. Eucalyptol**, 28. trans 2-hexenal, **30. beta-ocimene**, 31. n-Hexyl acetate, 36. cis 3 hexenil acetate, 41. hexanol, 42. trans-3 hexenol, 43. cis 3 hexenol, 46. trans 2 hexenol, 49. n-Valeric acid cis-3-hexenyl ester, 51. Copaene, **52. beta-linalool**

<i>Volatile compounds</i>	<i>Descriptor</i>	<i>Nasal Threshold (ppb)</i>	<i>Post nasal Threshold (ppb)</i>	<i>Reference</i>
pentil acetate	fruits, banana, sweet	-	0,026-37,0 <sup>n</sup>	Ruth, 1986
hexanal	fruity, apple, herbal	300 <sup>d</sup>	73 <sup>d</sup> , 60 <sup>l</sup>	<sup>d</sup> Guth & Grosh, 1990; Morales et al., 1999
1-pentenil acetate	fruity	-	-	
cis 3-hexenal	green, herbal	1,7 <sup>a</sup>	1,2 <sup>a</sup> , 3,0 <sup>l</sup>	Reiners & Grosh, 1998; <sup>l</sup> Morales et al., 1999;
trans 2-hexenal	fresh herbal	424 <sup>a</sup>	257 <sup>a</sup> , 1200 <sup>l</sup>	<sup>a</sup> Reiners & Grosh, 1998; <sup>l</sup> Morales et al., 1999
cis 2-pentenol	green	-	1500 <sup>h</sup>	<sup>h</sup> Morales & Aparicio, 1996;
hexanol	fruits, banana	-	400 <sup>h</sup>	<sup>h</sup> Morales & Aparicio, 1996;
trans 3-hexenol	green herbal	-	1500 <sup>r</sup>	<sup>r</sup> Aparicio e Morales, 1998;
cis 3-hexenol	green leaf	1100 <sup>a</sup>	364 <sup>a</sup> , 6000 <sup>r</sup>	<sup>a</sup> Reiners & Grosh, 1998; <sup>r</sup> Aparicio & Morales, 1998;
cis 2-hexenol	green herbal	-	10000 <sup>h</sup>	<sup>h</sup> Morales & Aparicio, 1996;

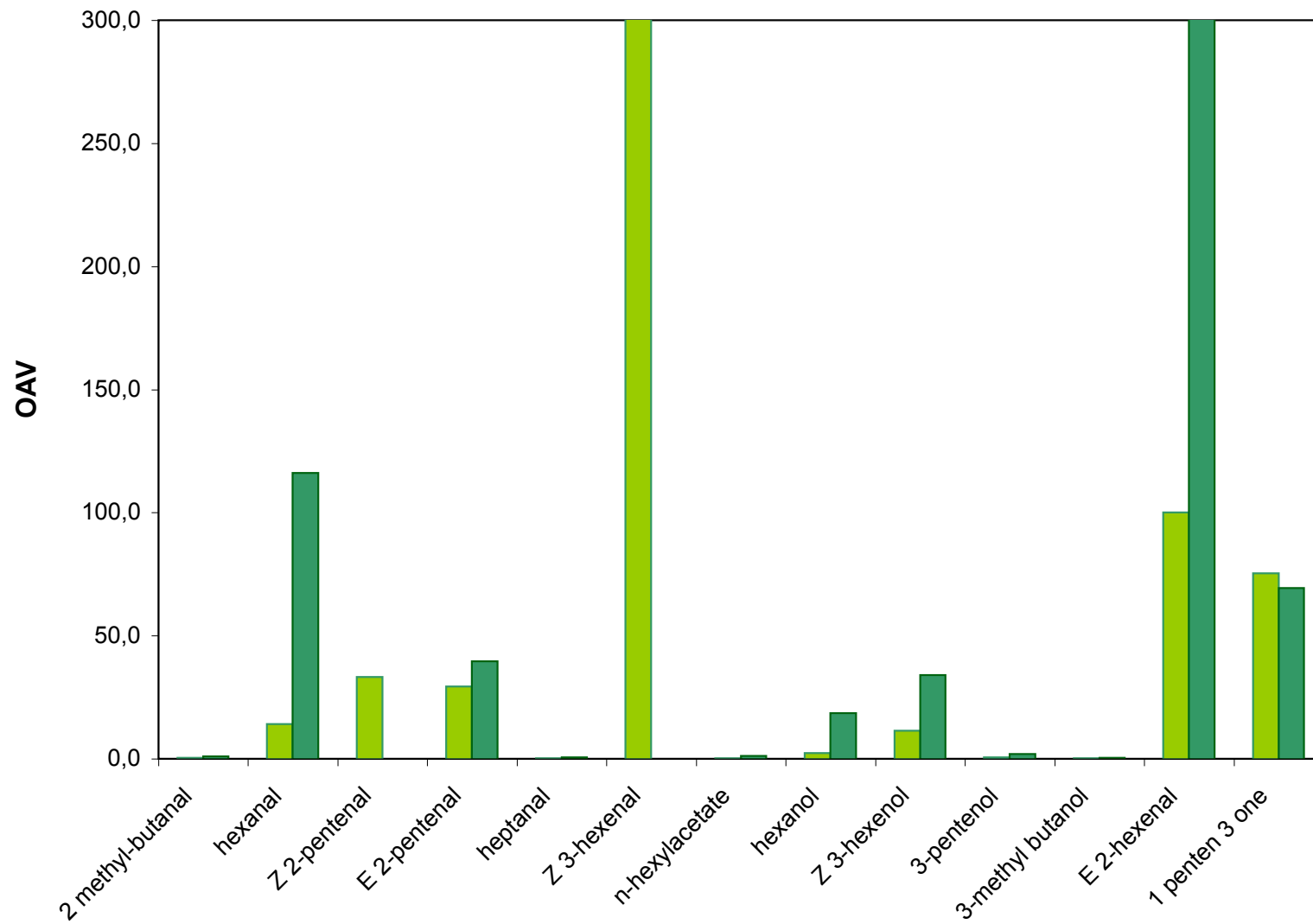
Nasal and post-nasal threshold reported for some of the volatile compounds characterizing the flavour of extra virgin olive oils

# Ravece (pomodoro) vs Coratina (mandorla) (ppm)

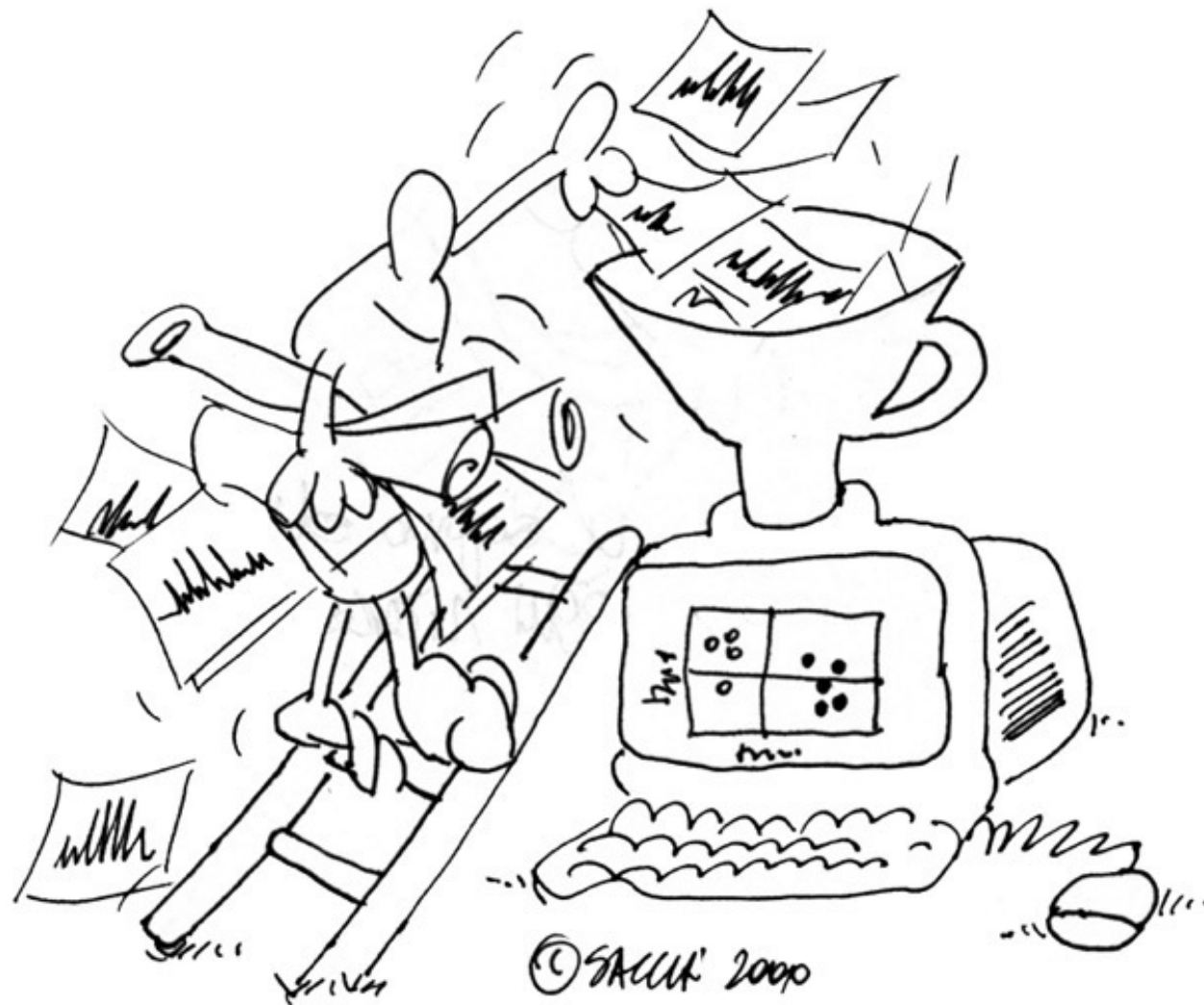




# Ravece vs Coratina (OAV)

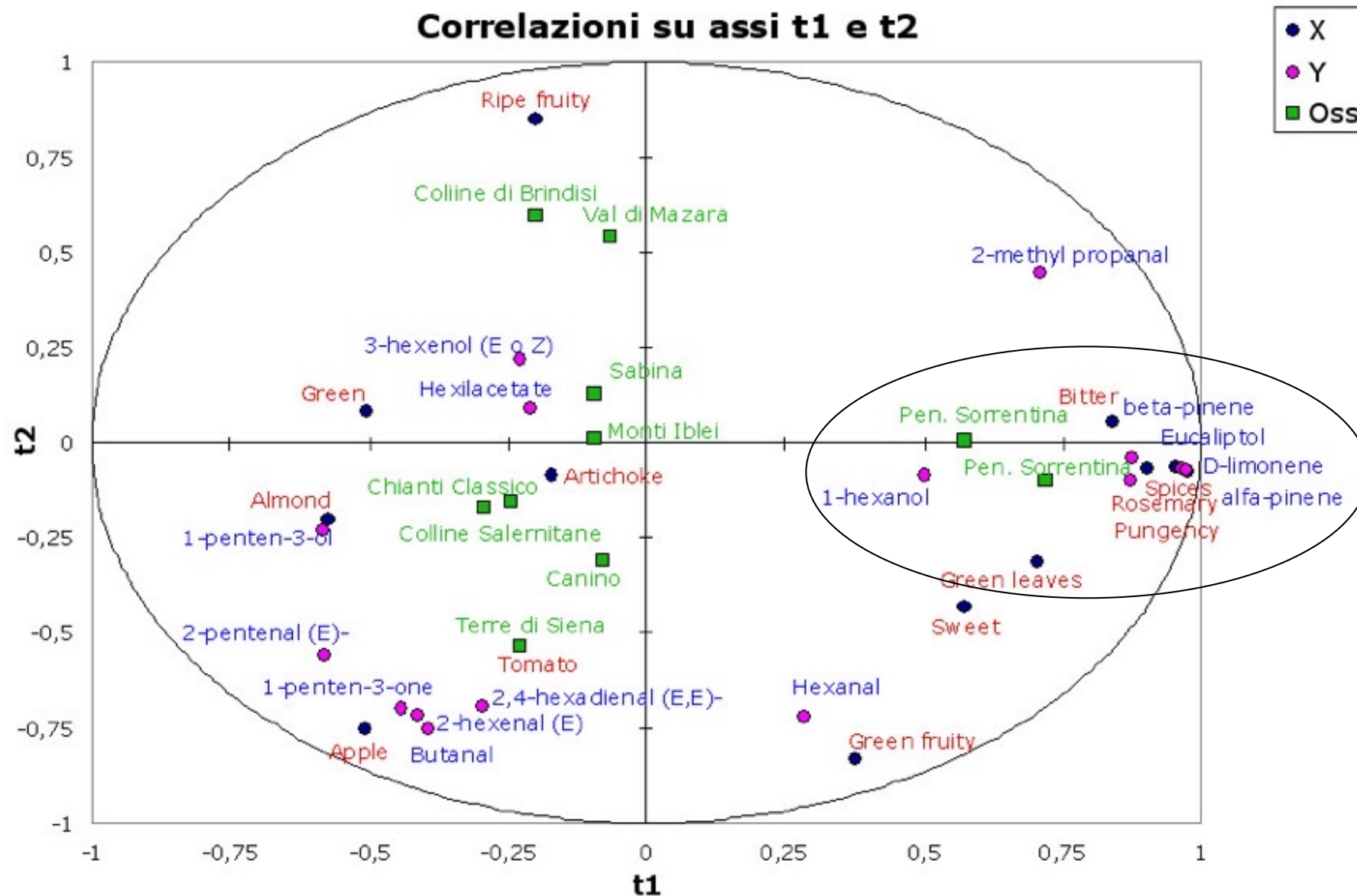


# Chemimetria (analisi statistica multivariata)



# *Odor Activity Value* (OAV)

$$\text{OAV} = \frac{\text{Concentrazione rilevata (mg/Kg)}}{\text{Odor treshold (soglia, mg/Kg)}}$$



Partial Least Square (PLS) performed on volatiles (OAV, blue) and sensory data (red)





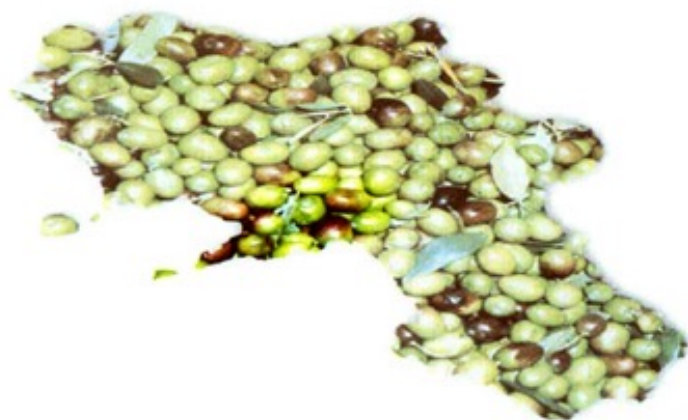






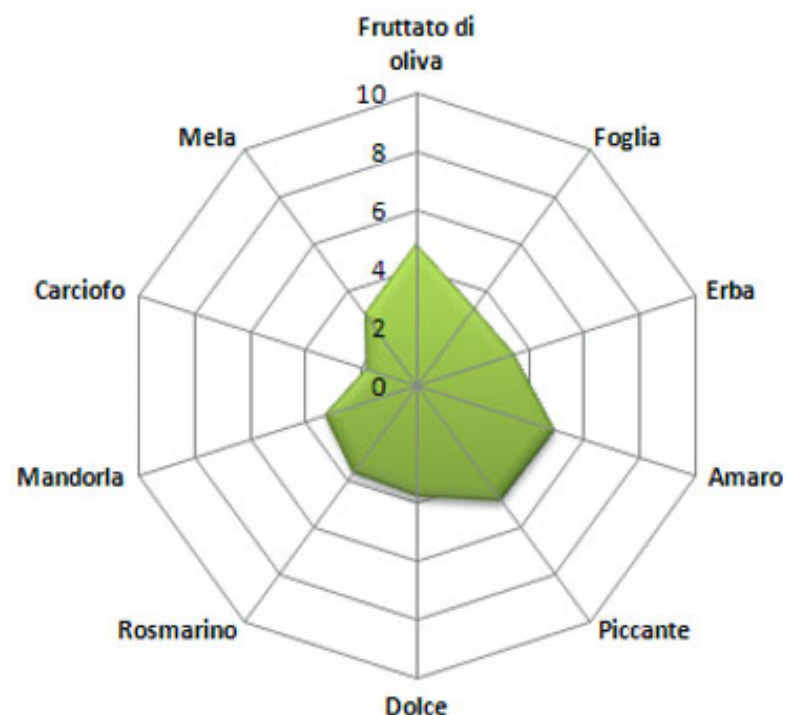
Regione Campania  
Assessorato Agricoltura  
Servizio Sperimentazione, Informazione,  
Ricerca e Consulenza in Agricoltura (S.E.R.C.A.)

# L'Olio della Penisola Sorrentina



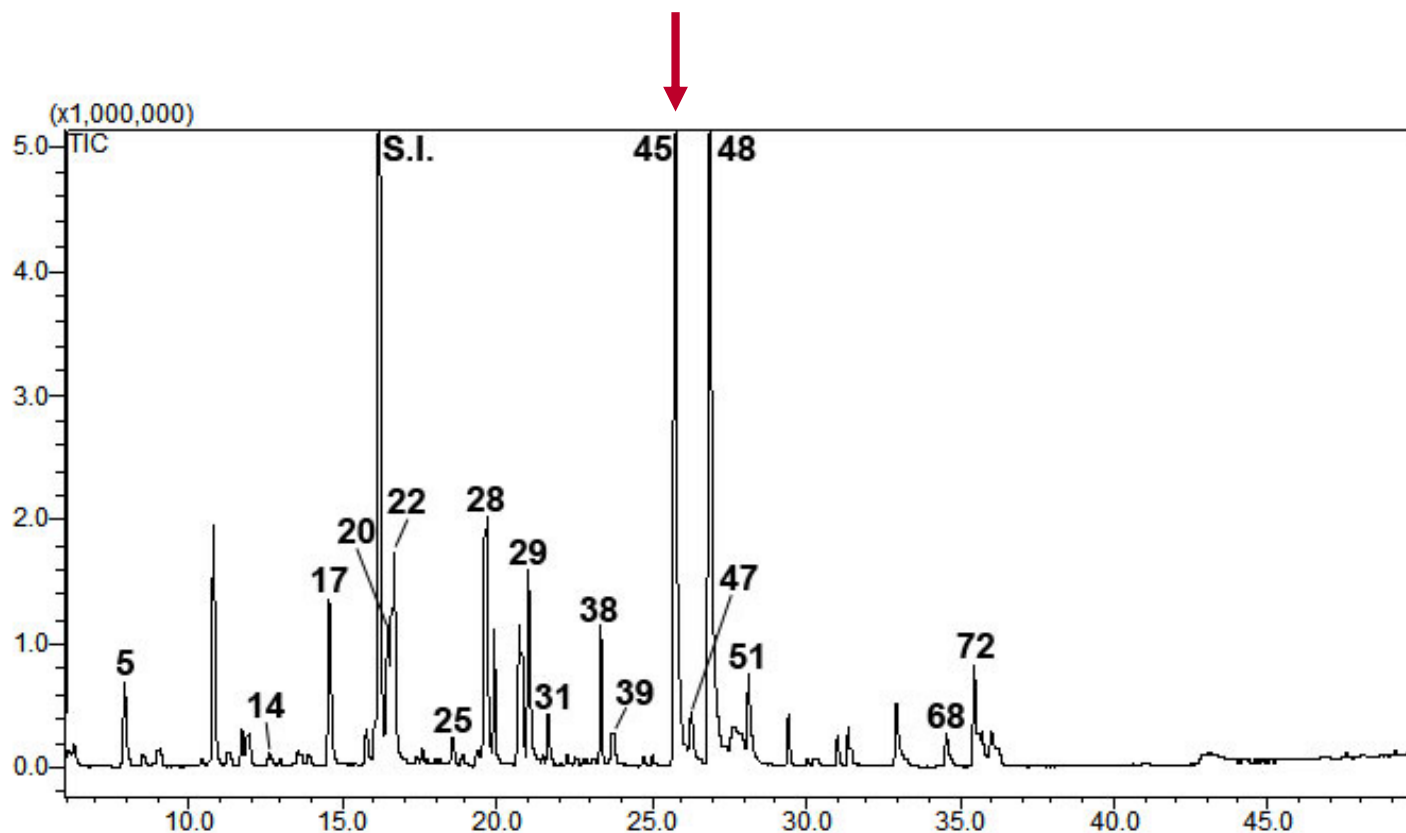
1997

Collana di monografie  
Gli Oli della Campania



Tipici sentori di “rosmarino”  
nell’olio della varietà  
Minucciola (Oliva da Olio,  
Ogliarola sorrentina)

**Cromatogramma della corrente ionica totale (TIC) ottenuto mediante analisi DHS-GCMS di un campione di olio DOP Penisola Sorrentina (2007)**



Identificazione dei picchi: **5.** ottano; **14.** etanolo; **17.** 3-pentanone; **20.**  $\alpha$ -pinene; **22.** 1-penten-3-one; **25.** canfene; **28.** esanale; **29.**  $\beta$ -pinene; **31.**  $\beta$ -fellandrene; **38.** 3-pentenolo; **39.**  $\beta$ -mircene; **45.** **D-limonene**; **47.** **eucaliptolo**; **48.** *trans*-2-esenale; **51.** *cis*- $\beta$ -ocimene; **68.** *cis*-3-esenolo; **72.** *trans*-2-esenolo.



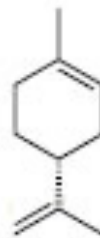
## Alcune molecole associate a note di erbe aromatiche e balsamiche



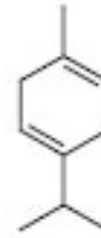
**20.**  $\alpha$ -pinene



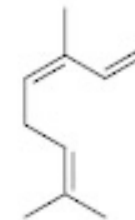
**29.**  $\beta$ -pinene



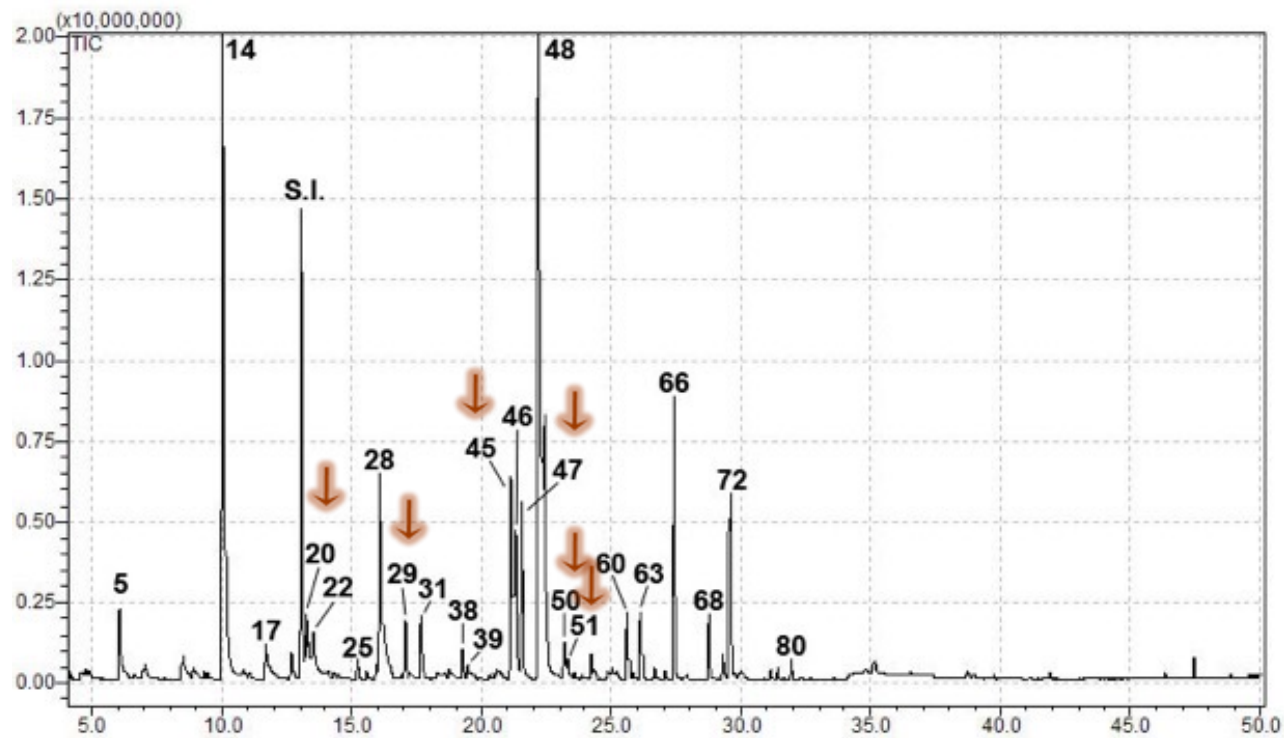
**45.** D-limonene



**50.**  $\gamma$ -terpinene



**51.** (Z)- $\beta$ -ocimene

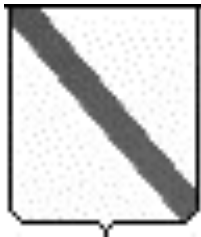


# Effetto dell'attacco della mosca delle olive sulla qualità dell'olio vergine



**Nunzio Esposito, Maria Luisa Ambrosino, Antonello Paduano, Raffaele Sacchi**

*Dipartimento di Scienza degli Alimenti, Facoltà di Agraria, Portici (Napoli)*

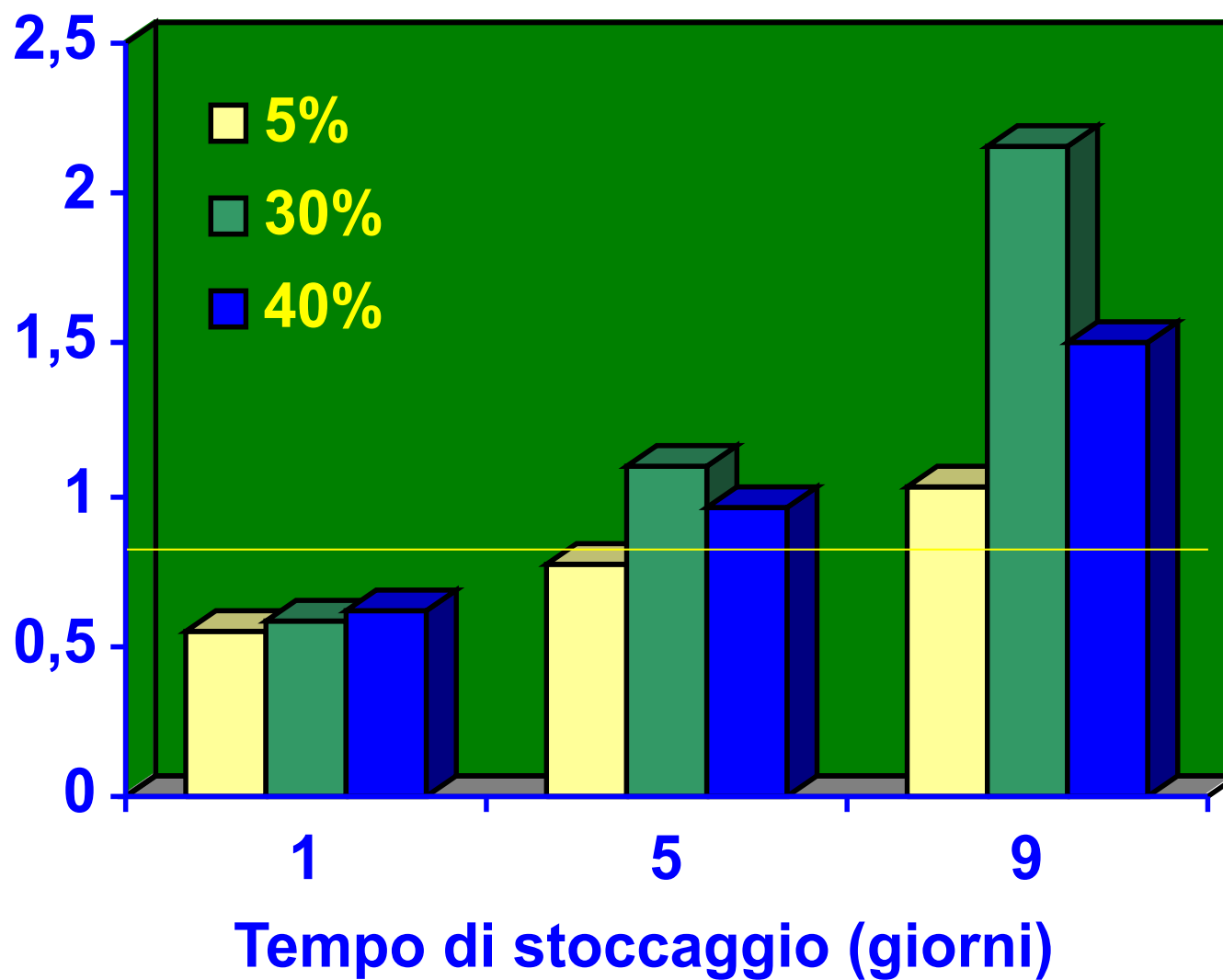


**Grazia Stanzione**

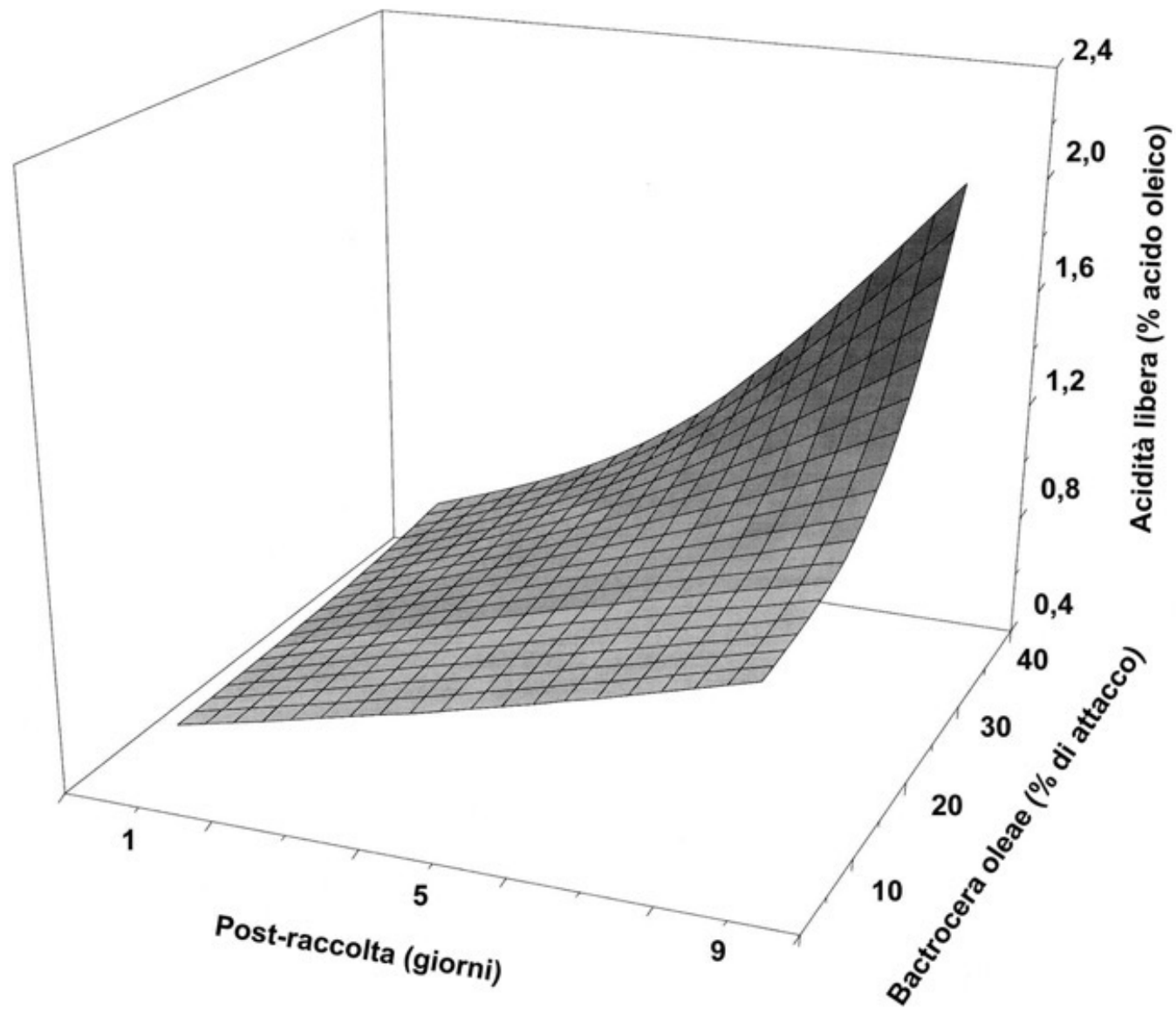
*STAPA-CEPICA, Castellammare di Stabia (Napoli)*

Lavoro realizzato negli anni 2000-2001

## Acidità Libera e infestazione (%) da mosca olearia

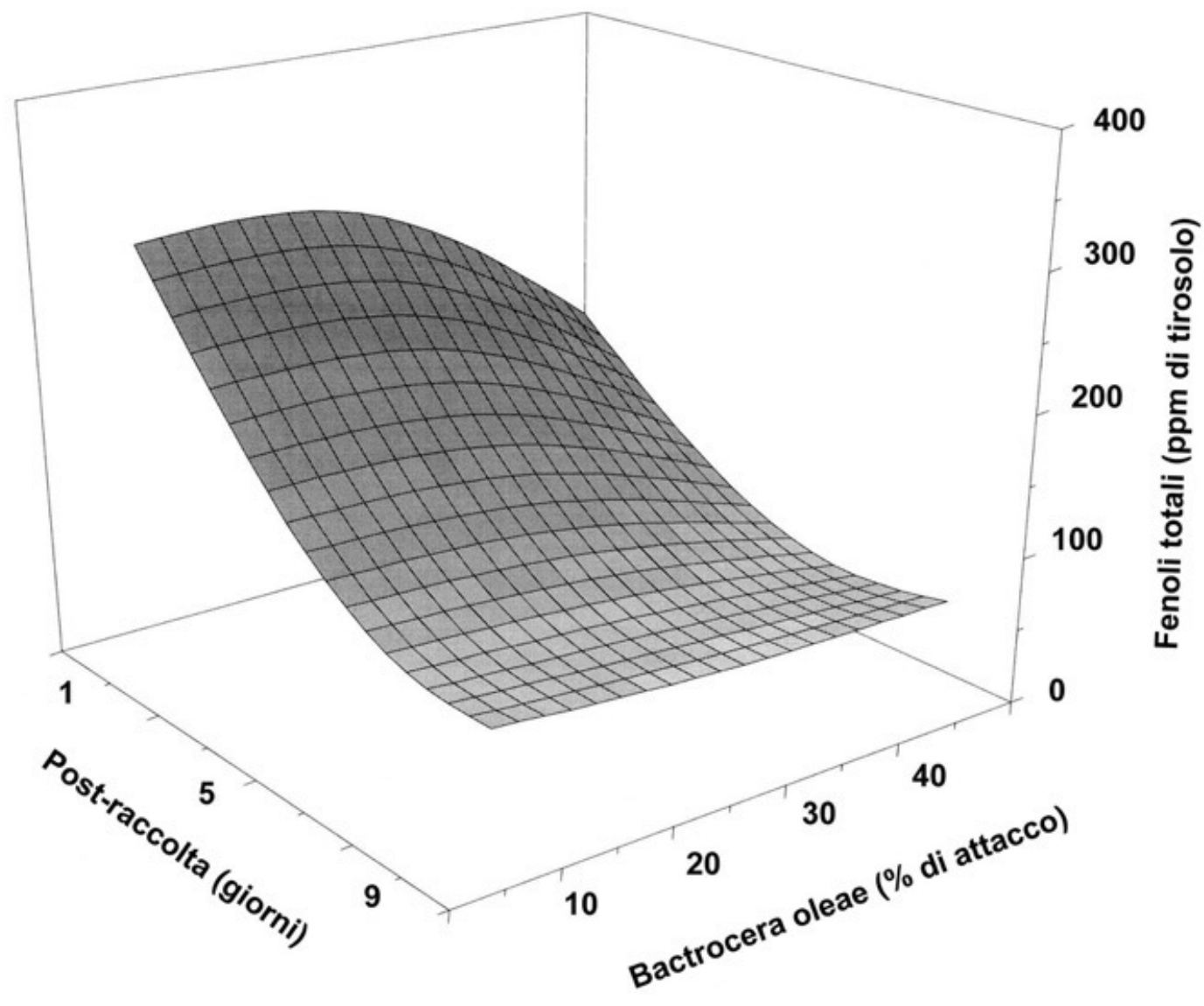


# Evoluzione dell'acidità libera





# Evoluzione dei fenoli totali









## Principali composti volatili identificati e quantificati in alcuni campioni di oli DOP “Penisola Sorrentina” (2005-2007)

n° picco	r.t. (min)	Nome composto	$\mu\text{g/kg}^1$						$\mu\text{g/kg}^1$	
			Campione 1	Campione 2	Campione 3	Campione 4	Campione 5	Campione 6	Campione 7	Campione 8
5	6,1	Ottano	396,7	231,5	155,8	121,6	94,7	79,9	161,7	245,4
14	10,0	Etanolo	3942,3	3390,4	3838,1	3956,8	764,0	376,7	25,8	54,5
17	11,7	3-pentanone	219,3	586,0	255,4	103,8	201,1	112,6	310,1	371,5
20	13,3	$\alpha$ -pinene	319,9	n.r.*	35,1	996,5	n.r.	240,9	251,7	261,4
22	13,5	1-penten-3-one	418,9	1862,5	321,7	433,7	770,5	247,9	362,4	361,8
25	15,2	Canfene	87,2	n.r.	n.r.	238,3	295,6	23,6	39,9	25,6
28	16,1	Esanale	1416,1	2939,5	1094,5	1130,0	1345,0	1395,4	359,7	326,2
29	17,1	$\beta$ -pinene	262,3	n.r.	23,2	522,3	n.r.	1407,5	584,1	596,9
31	17,7	$\beta$ -fellandrene	322,8	n.r.	n.r.	502,9	n.r.	390,6	83,3	88,8
38	19,3	3-pentenolo	130,1	396,9	200,5	122,5	n.r.	110,1	144,1	144,6
39	19,5	$\beta$ -mircene	69,1	n.r.	17,2	471,3	n.r.	407,1	42,2	39,6
45	21,2	D-limonene	938,5	127,4	255,7	2413,7	25,2	11440,9	1633,0	1584,4
46	21,3	3-metilbutanolo	830,1	168,3	293,8	299,3	195,3	n.r.	n.r.	n.r.
47	21,6	Eucaliptolo	803,2	169,3	126,9	2279,2	40,2	339,2	124,6	121,9
48	22,2	trans -2-esenale	4868,5	34458,3	27684,0	15289,2	16039,8	21471,5	2403,4	2376,7
50	23,2	$\gamma$ -terpinene	227,5	136,9	n.r.	371,8	63,3	1402,1	n.r.	n.r.
51	23,3	cis - $\beta$ -ocimene	78,0	97,6	259,4	1035,5	354,7	214,6	18,1	29,4
60	25,6	4,8-dimetil-1,3,7-nonatriene	268,6	394,0	904,2	934,2	3739,9	761,1	n.r.	n.r.
66	27,4	Esanolo	1044,0	2667,6	3643,6	1703,7	1144,8	1258,2	145,9	129,5
68	28,8	cis -3-esenolo	247,9	800,1	870,5	554,9	580,5	520,2	67,8	65,0
72	29,6	trans -2-esenolo	673,0	6893,9	5726,1	2519,3	1169,4	1866,4	166,1	140,6

<sup>1</sup> valore dato dalla media di tre repliche

\* n.r.=non rilevato





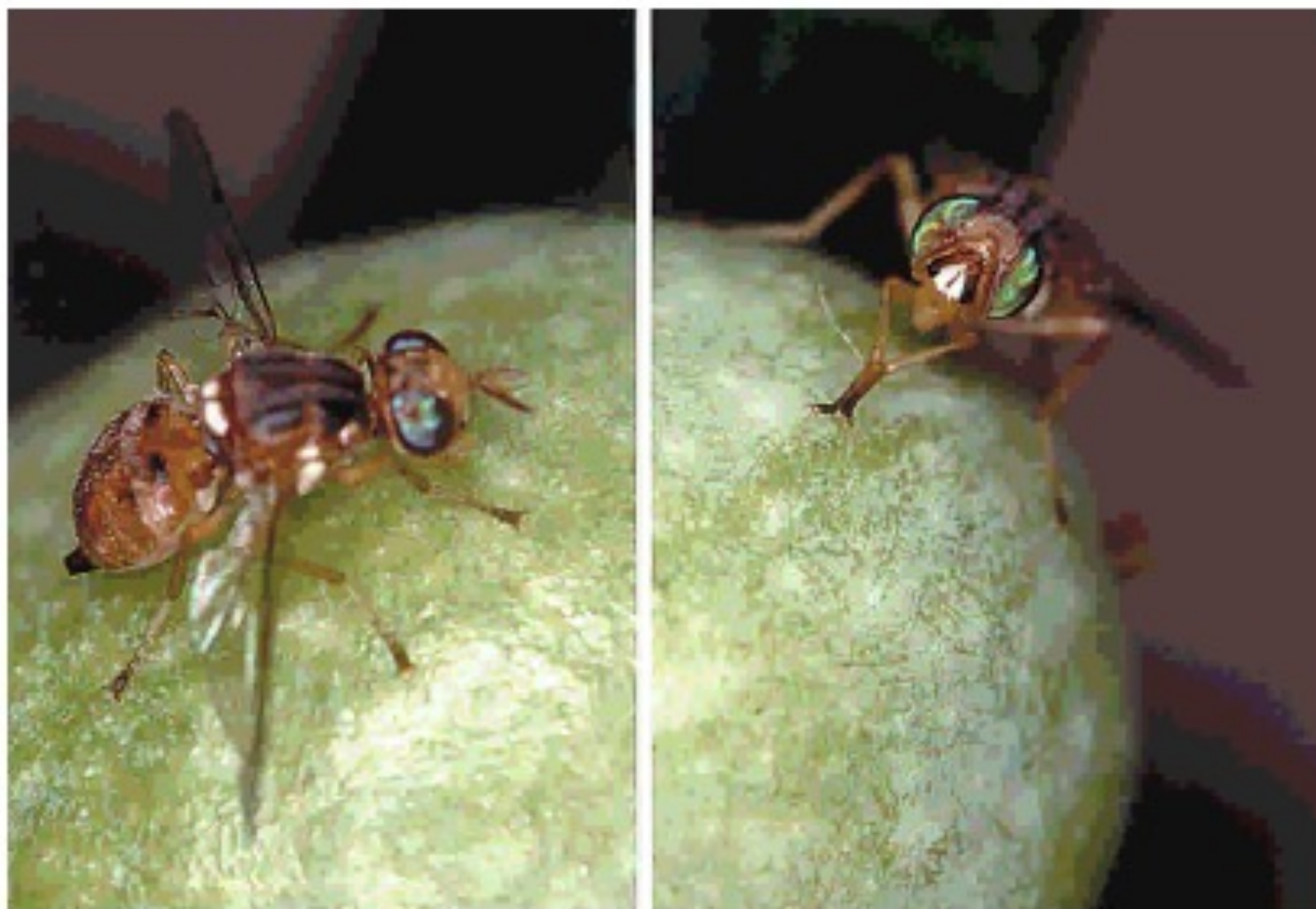
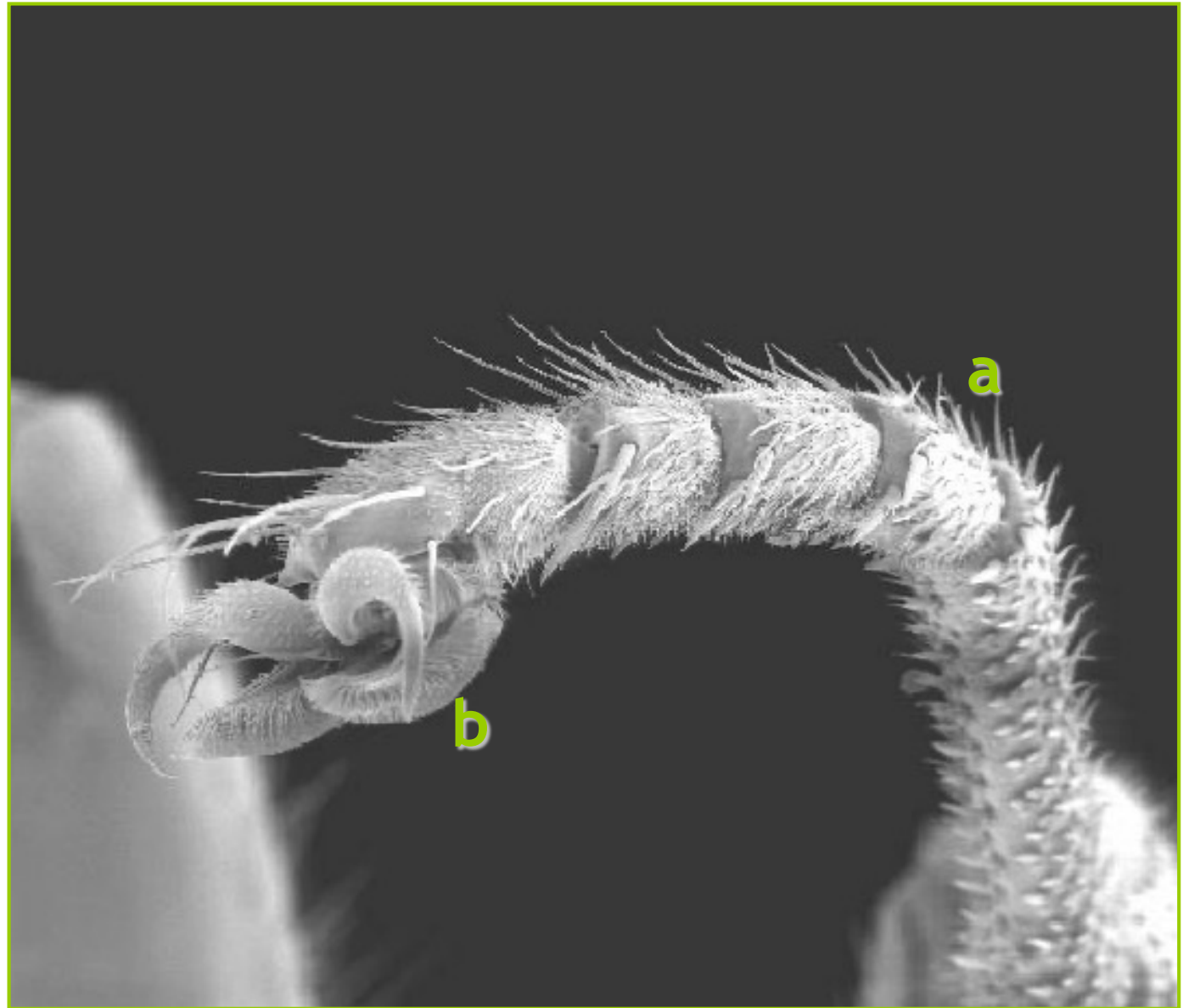


Fig. 1 - *Bactrocera oleae* Gmel. Female on an olive, exploring the fruit surface (on left), and rubbing prothoracic tarsi (as it were washing hands).

**Il tarso presenta 5  
articoli:**

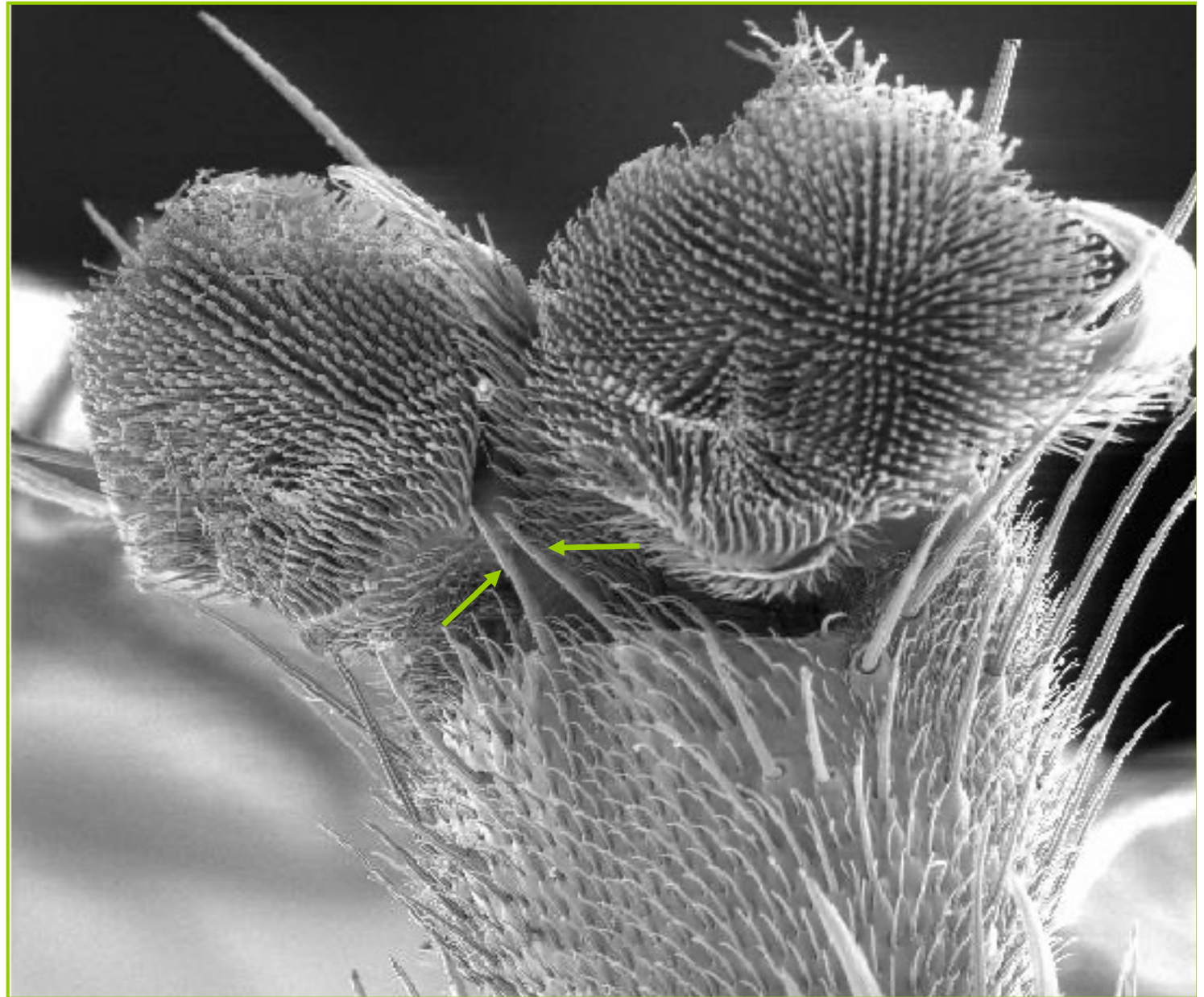
- il primo (a) non  
entra in contatto  
con il substrato
- il quinto (b) è il  
più ampio e  
contiene numerosi  
sensilli



300  $\mu\text{m}$

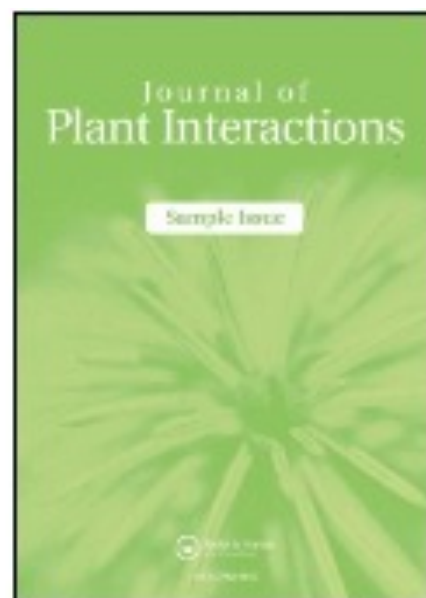
(Thanks to Prof. De Cristoforo, 2008)

Sul quinto  
tarsomero sono  
presenti  
chemiorecettori  
da contatto, i  
sensilli “C”



100  $\mu\text{m}$





## Journal of Plant Interactions

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpptitle-content=1716100758>

### Host-locating response by the aphid parasitoid

#### **Aphidius ervi** to tomato plant volatiles

Raffaele Sasso <sup>a</sup>; Luigi Iodice <sup>b</sup>; Maria Cristina Digilio <sup>b</sup>; Andrea Carretta <sup>c</sup>; Luigi Ariati <sup>d</sup>; Emilio Guerrieri <sup>a</sup>

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<sup>c</sup> Idrocons srl, Rivalta Scrivia, Italy

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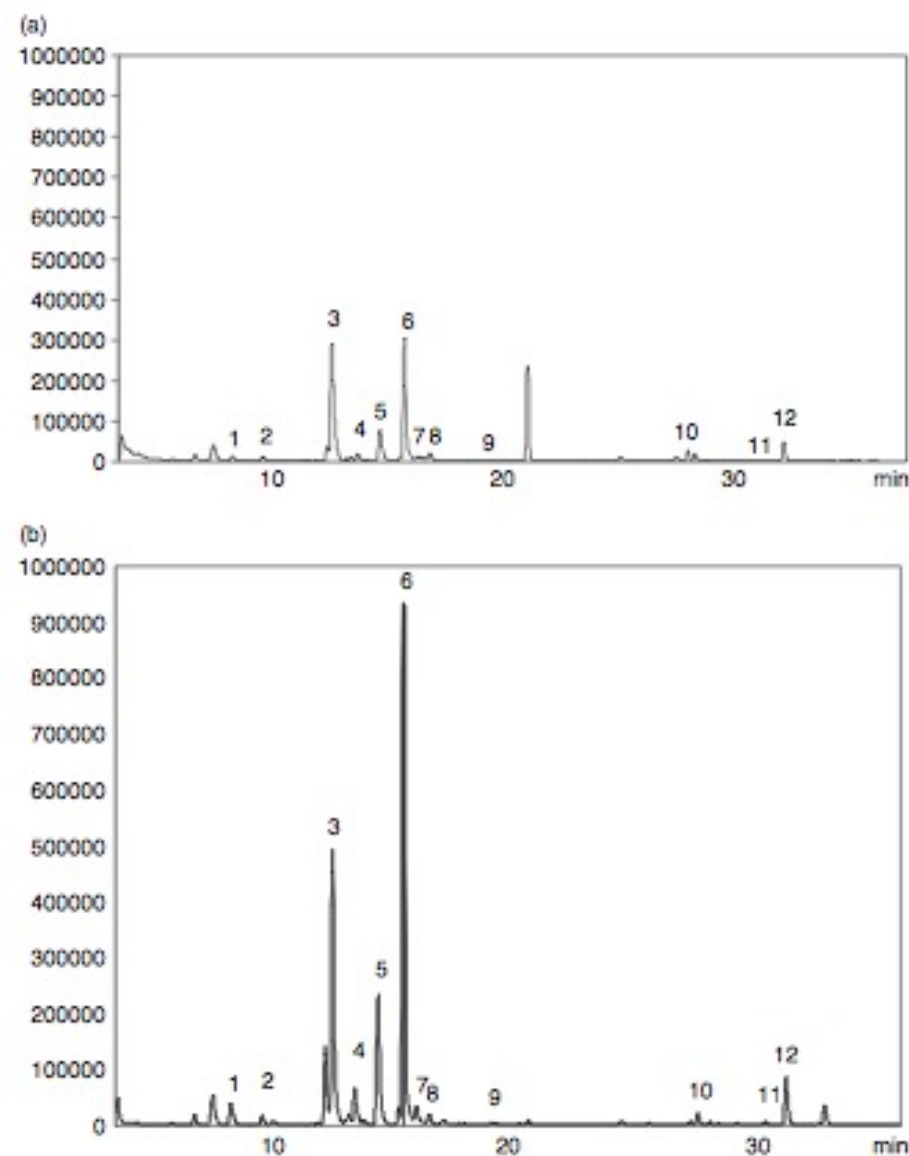
Andrea, Ariati, Luigi and Guerrieri, Emilio (2007) 'Host-locating response by the aphid parasitoid **Aphidius ervi** to tomato plant volatiles', *Journal of Plant Interactions*, 2:3, 175 - 183

To link to this article: DOI: 10.1080/17429140701591951

URL: <http://dx.doi.org/10.1080/17429140701591951>

#### **Abstract**

The blend of volatile compounds emitted by tomato plants (*Solanum lycopersicum*) infested with the potato aphid (*Macrosiphum euphorbiae*) has been studied comparatively with undamaged plants and aphids themselves. Aphid-infested plants were significantly more attractive towards *Aphidius ervi* than undamaged plants and aphids themselves. Oriented response towards host-damaged plant, from which aphids were removed just before running the bioassay, did not differ from that recorded for infested plants. Collection of the volatiles and analysis by gas chromatography revealed only quantitative differences between uninfested and aphid-infested plants. Nine compounds,  $\alpha$ -pinene, (*Z*)-3-hexen-1-ol,  $\alpha$ -phellandrene, limonene, (*E*)- $\beta$ -ocimene, p-cymene, methyl salicylate, (*E*)- $\beta$ -caryophyllene and an unknown compound, were emitted at higher levels from aphid-infested plants than from undamaged control plants, whilst no differences were noted for hexanal, 6-methyl-5-hepten-2-one, and humulene (=  $\alpha$ -caryophyllene). Synthetic standards of these compounds were tested in wind tunnel bioassays and all elicited a significant increase in oriented flight and landings on the target by the aphid parasitoid *Aphidius ervi*. (*E*)- $\beta$ -caryophyllene resulted the most attractive towards female wasps. These results corroborate the hypothesis that the volatiles produced by the plant in response to aphid attack derive from both jasmonic and salicylic acid pathways, and are exploited by *A. ervi* as olfactory cues to locate its hosts.



non infestate

infestate

Figure 2. Chromatograms of volatile emissions collected by air-entrainment of head-space from (a) tomato plants uninfested and (b) infested for 7 days by *Macrosiphum euphorbiae*. Numbers indicate the identified peaks. 1 =  $\alpha$ -pinene, 2 = hexanal (partially overlapping the peak of (*Z*)-3-hexen-1-ol), 3 = unknown compound, 4 =  $\alpha$ -phellandrene, 5 = R/S limonene, 6 = (*E*)- $\beta$ -ocimene, 7 = *p*-cymene, 8 = *p*-dichlorobenzene (IS), 9 = 6-methyl-5-hepten-2-one, 10 = methyl salicylate, 11 = longifolene, 12 = (*E*)- $\beta$ -caryophyllene.



*Plant, Cell and Environment* (2008), **31**, 575-585.

## Significance of terpenoids in induced indirect plant defence against herbivorous arthropods

ROLAND MUMM<sup>1</sup>, MAARTEN A. POSTHUMUS<sup>2</sup> & MARCEL DICKE<sup>1</sup>

Laboratory of Entomology, Wageningen University, PO Box 8031, 6700 EH Wageningen, the Netherlands and <sup>2</sup>Laboratory of Organic Chemistry, Wageningen University, PO Box 8026, 6700 EG Wageningen, the Netherlands

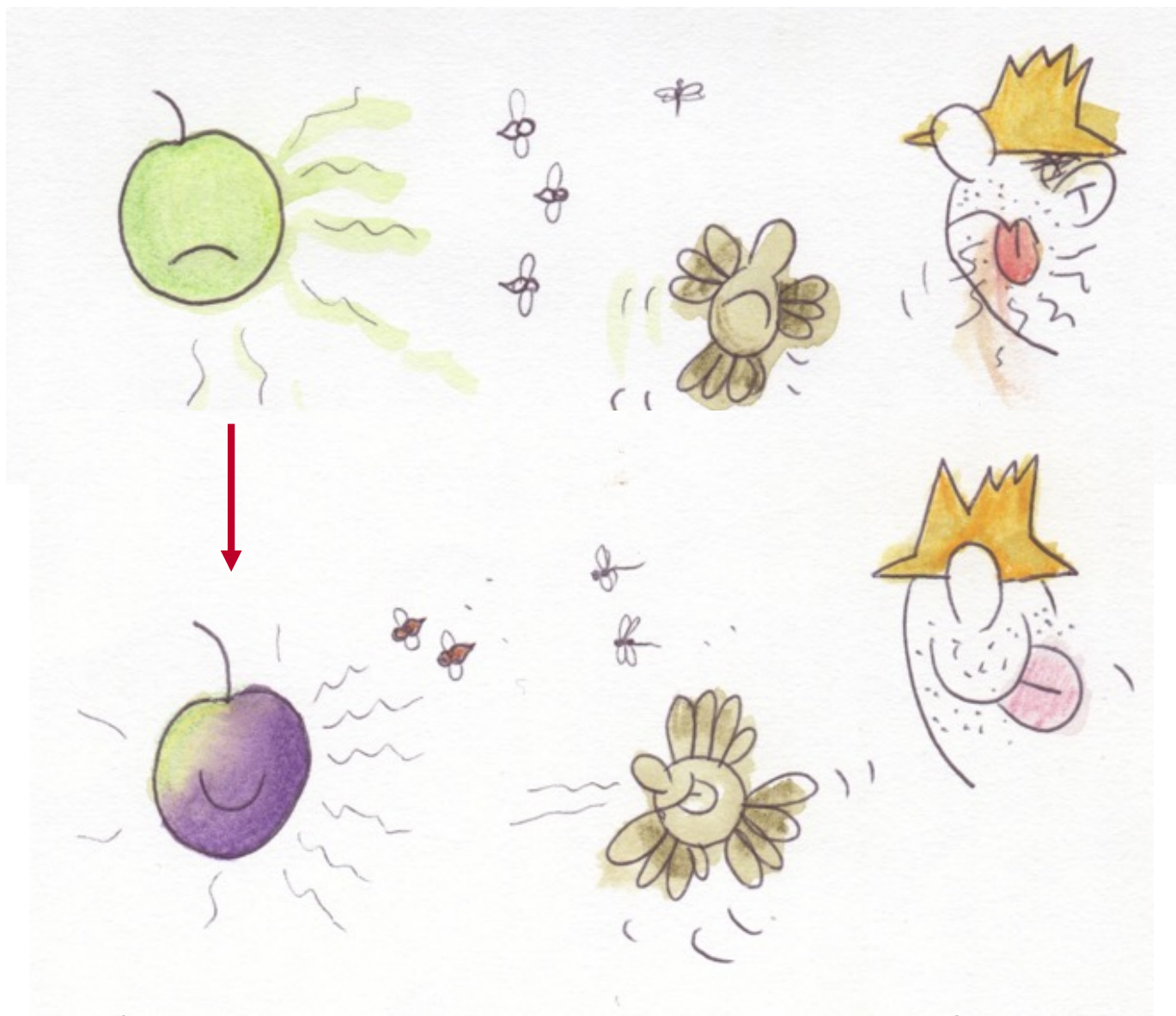
**“Many plants respond to arthropods with an induced emission of volatiles such as green leaf volatiles and terpenoids.**

**These herbivore-induced plant volatiles can attract carnivores, for example, predators and parasitoids.”**

E se la mosca stimolasse la produzione di aromi tipici nella minucciola (stress biotici)?

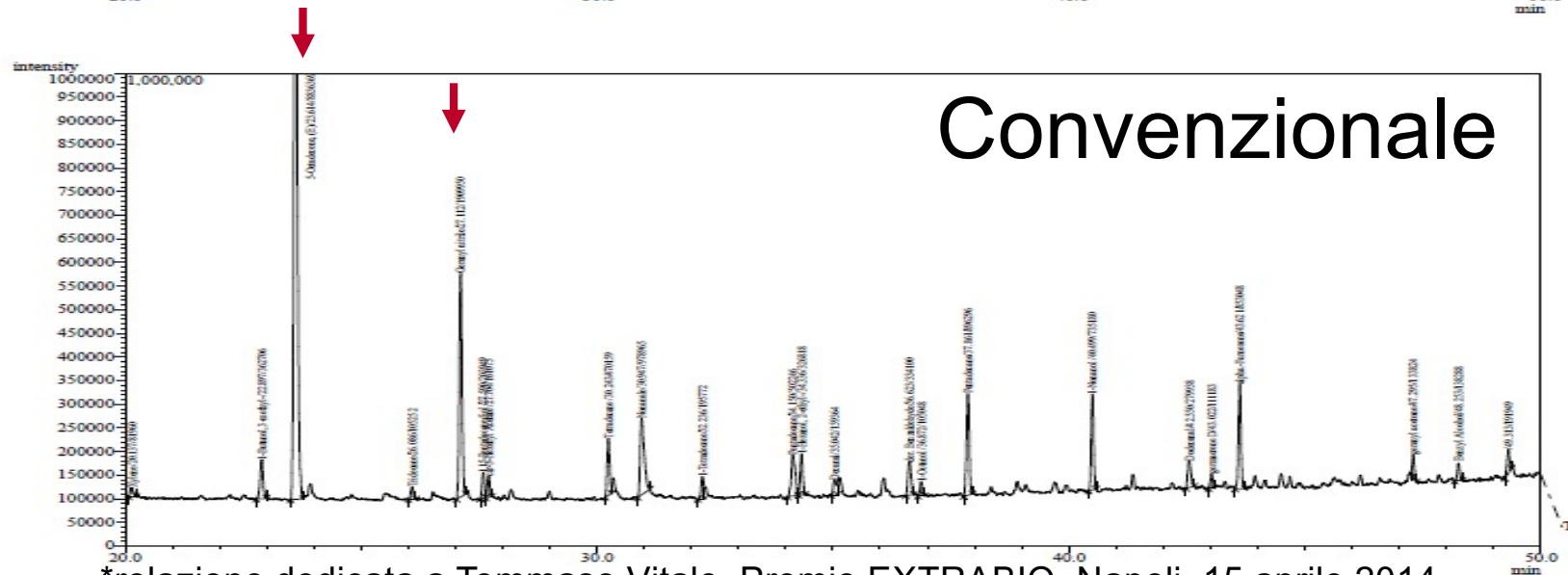
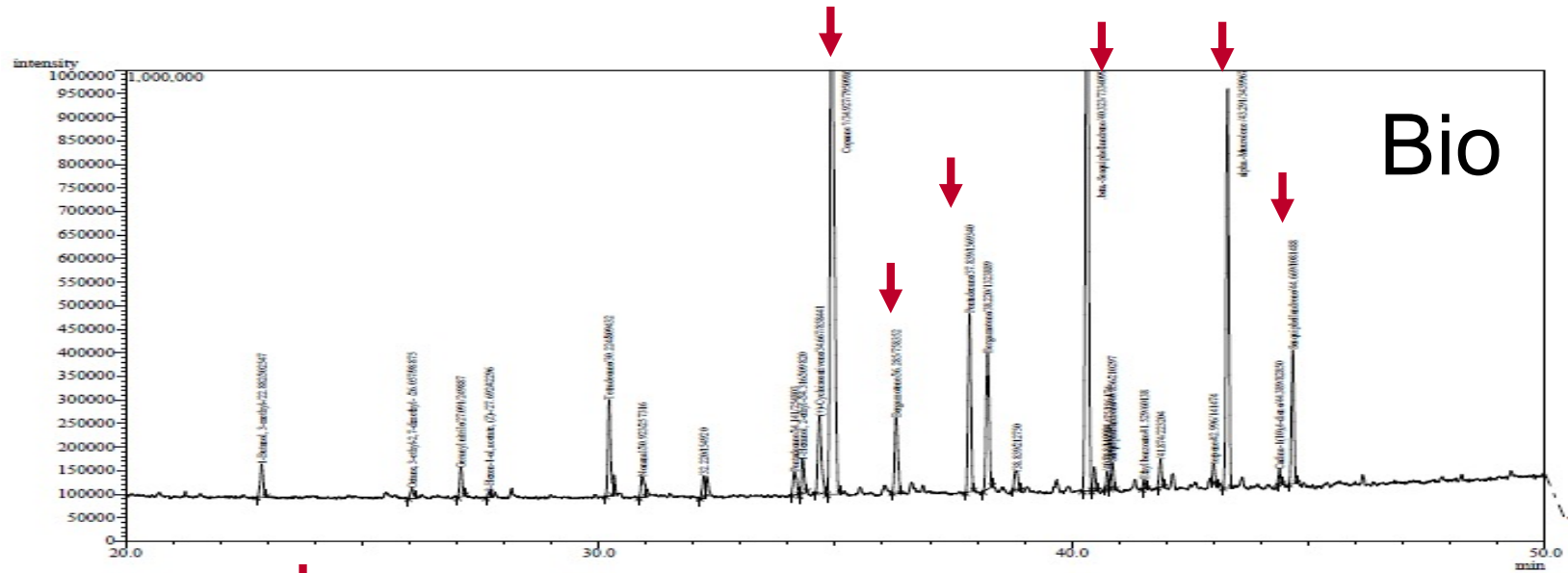


# Ruolo eco-fisiologico dei profumi dell'oliva (e dell'olio)



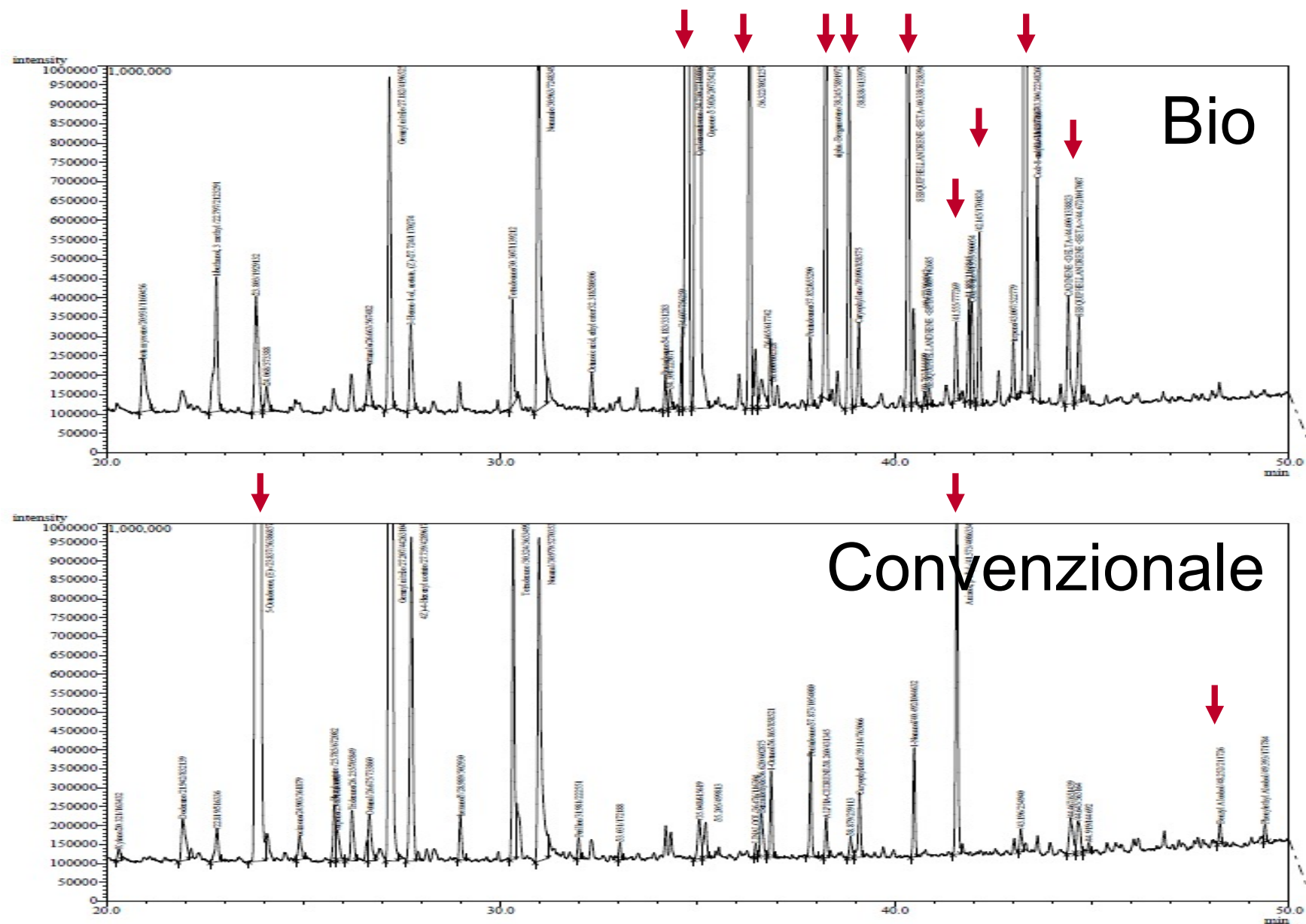
\*relazione dedicata a Tommaso Vitale, Premio EXTRABIO, Napoli, 15 aprile 2014

# Aromi emessi da olive sane (Minucciola, 2012)

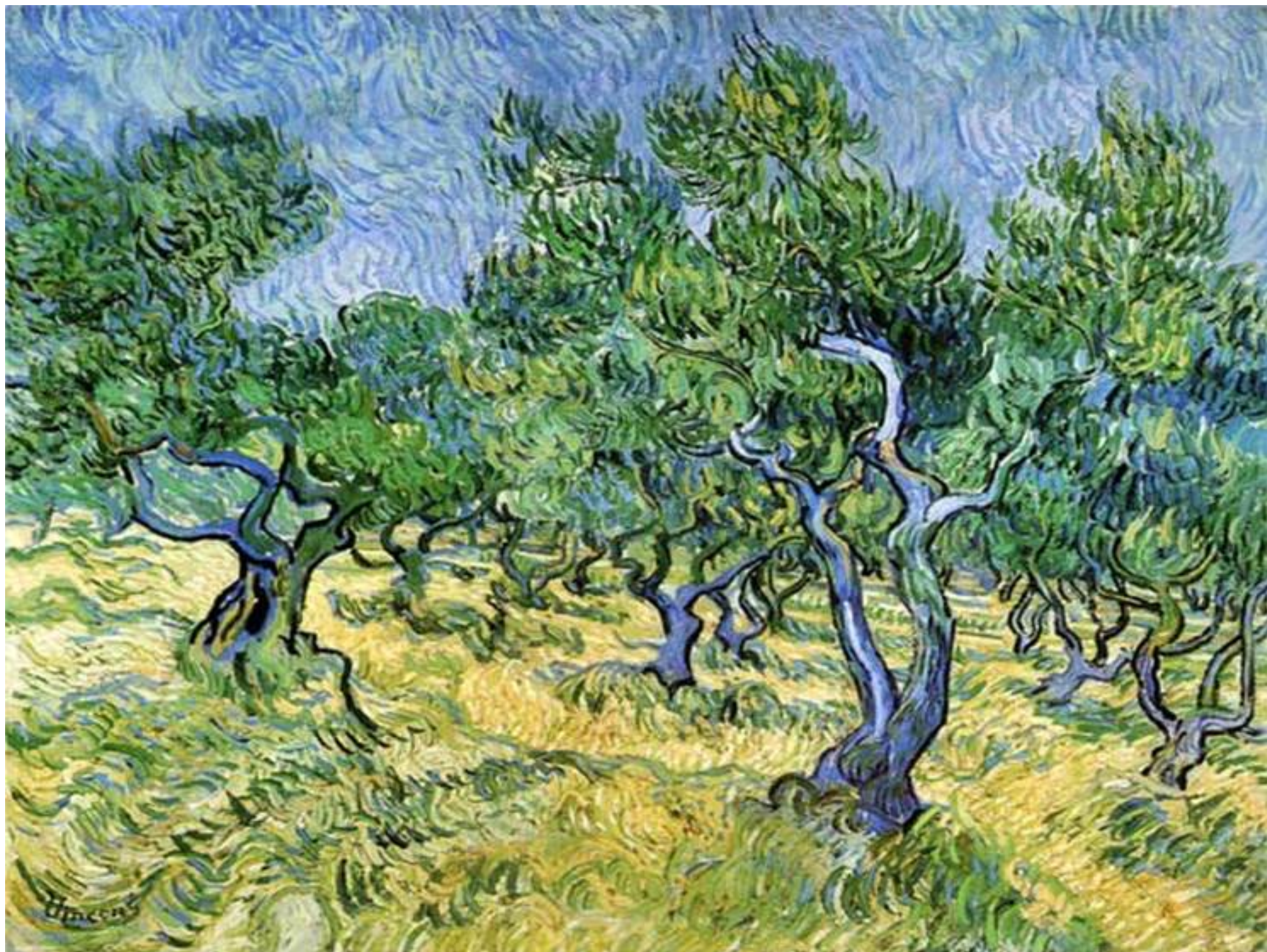


\*relazione dedicata a Tommaso Vitale, Premio EXTRABIO, Napoli, 15 aprile 2014

# Aromi emessi da olive sane (Ortice, 2012)







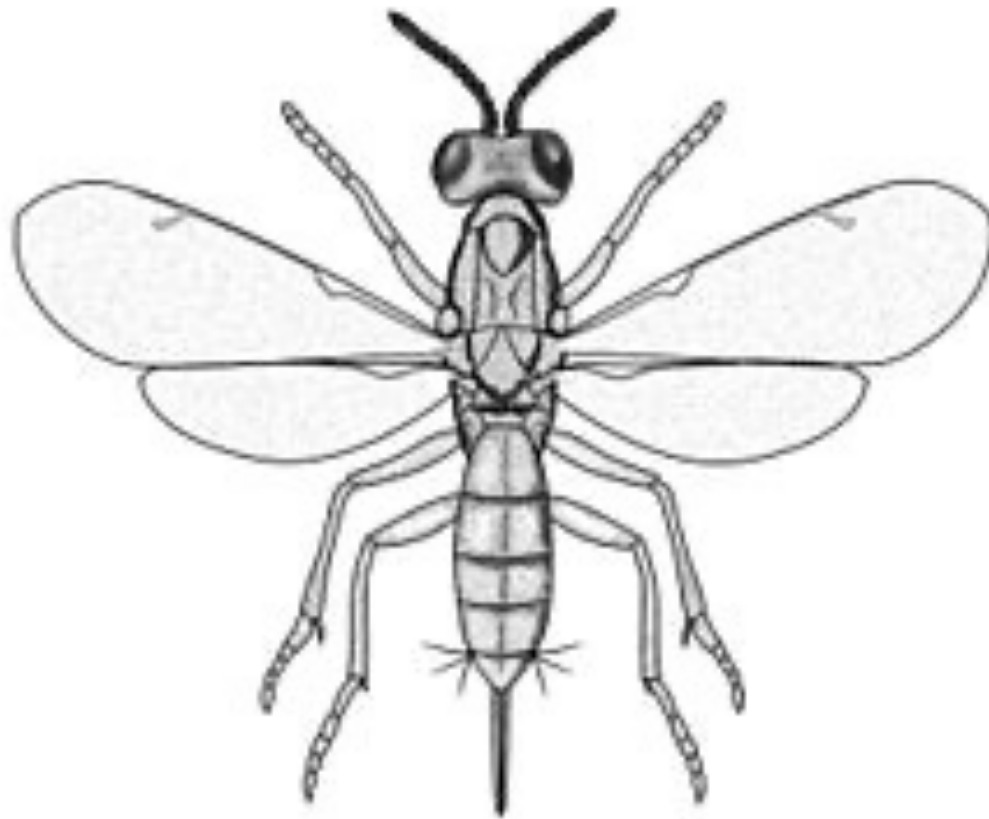








# Eupelmus Urozonus



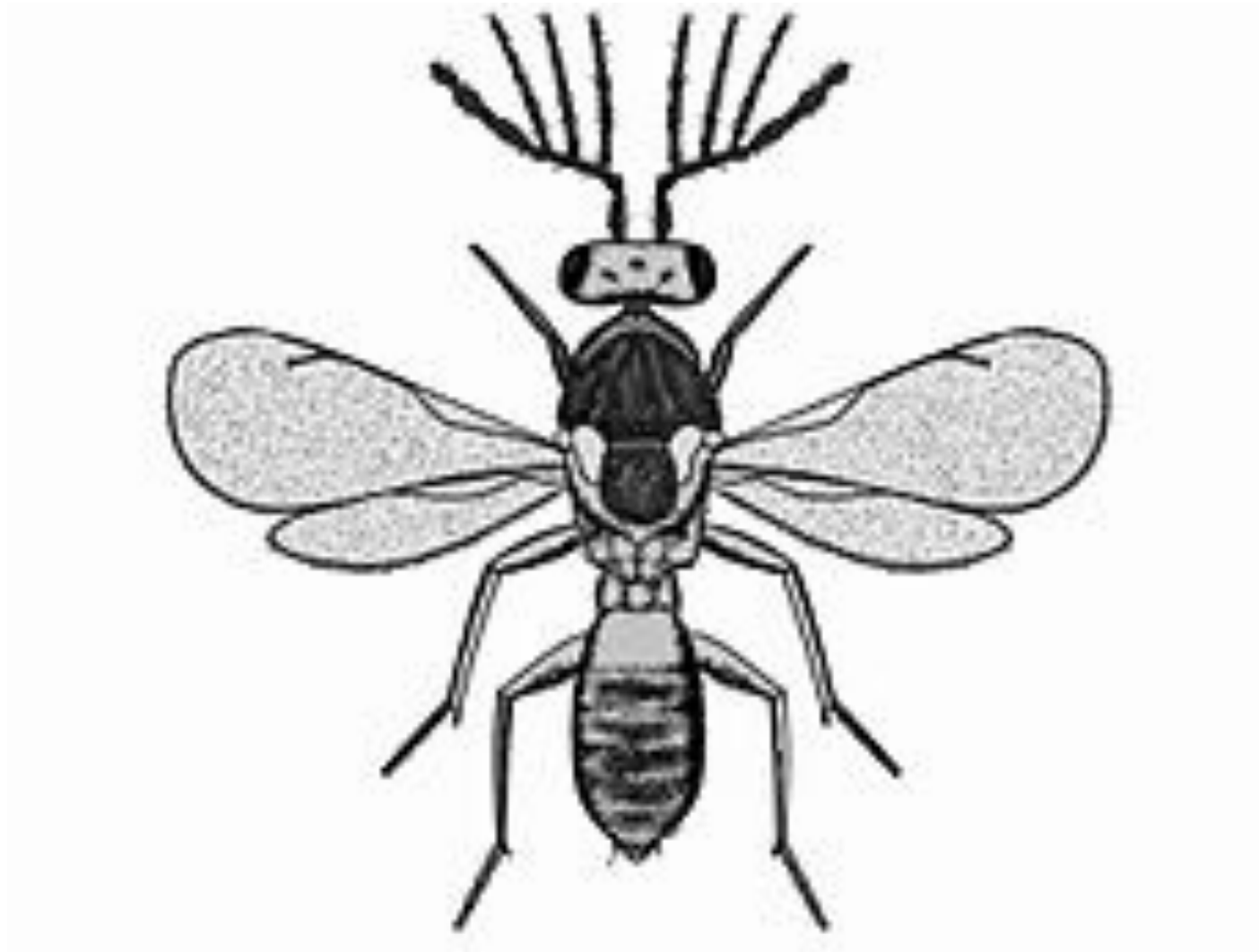




L'*inula viscosa* è attaccata dal *Myopites stylata*, un Dittero Tefritide galligeno.

Questo insetto rappresenta l'ospite svernante dell'*Eupelmus urozonus*, un parassitoide polifago degli Imenotteri Calcidoidi che svolge 2-3 generazioni all'anno sulla mosca delle olive.

Dal momento che l'*Eupelmus* è il più attivo antagonista naturale della mosca delle olive, la diffusione dell'*Inula* negli incolti delle aree olivetate può contribuire al controllo del fitofago nei programmi di lotta integrata e biologica.



*Pnigalio mediterraneus*











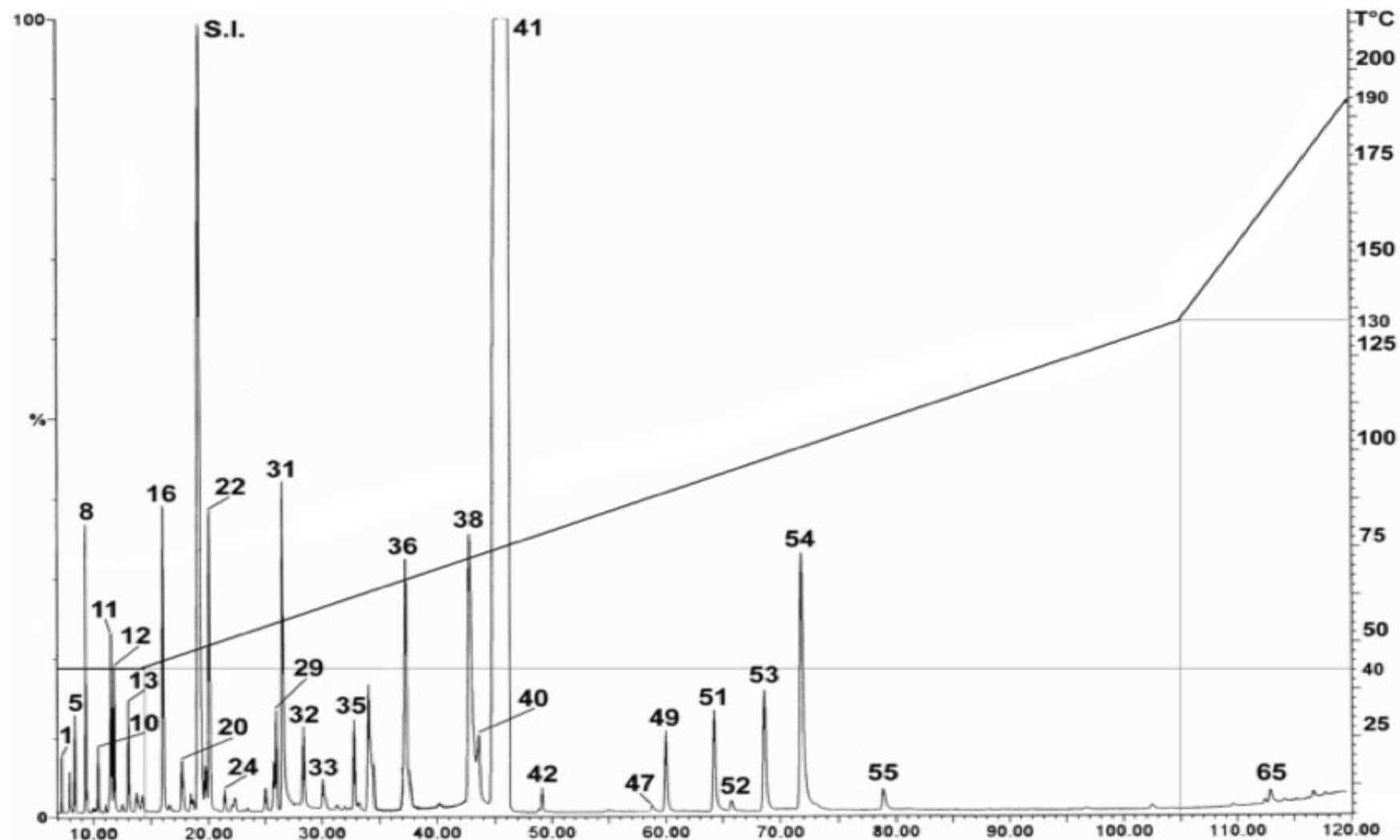
Introduzione di **Tecnologie**  
**Ecocompatibili** per l'ottimizzazione  
delle produzioni **Olivicolo-olearie** del  
Basso Cilento e la loro valorizzazione

*GAL CASACASTRA, PSR, Misura 124*  
*sportello.olio@libero.it*

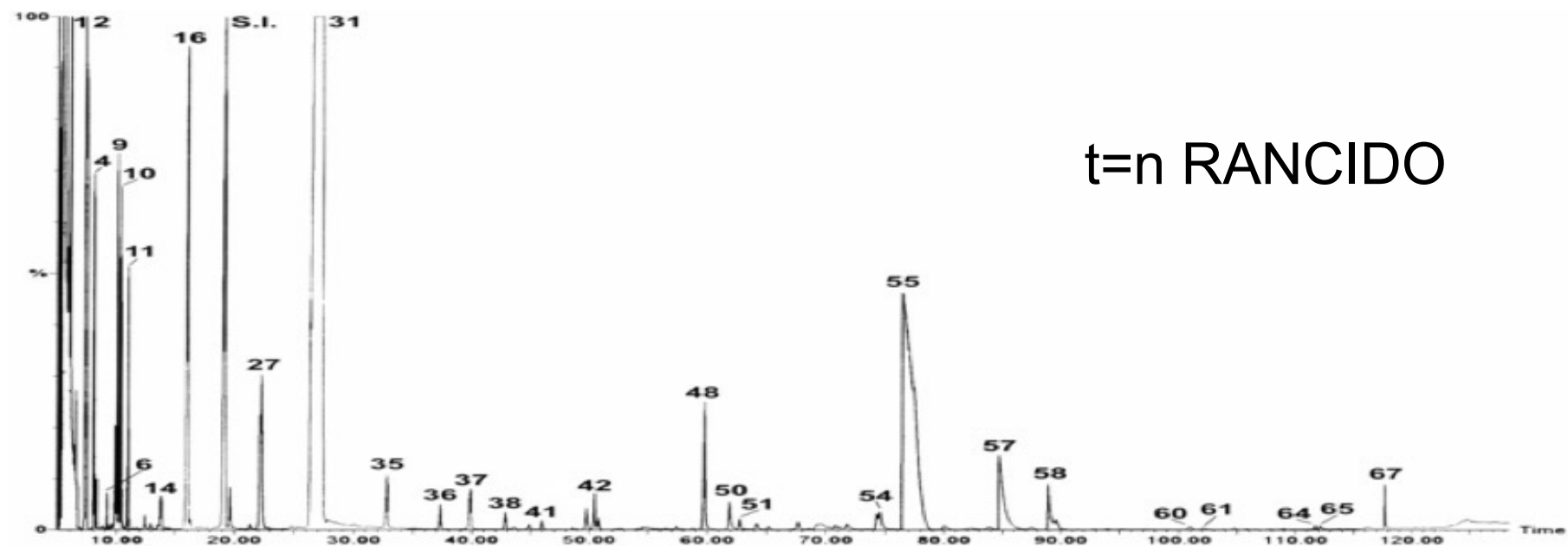
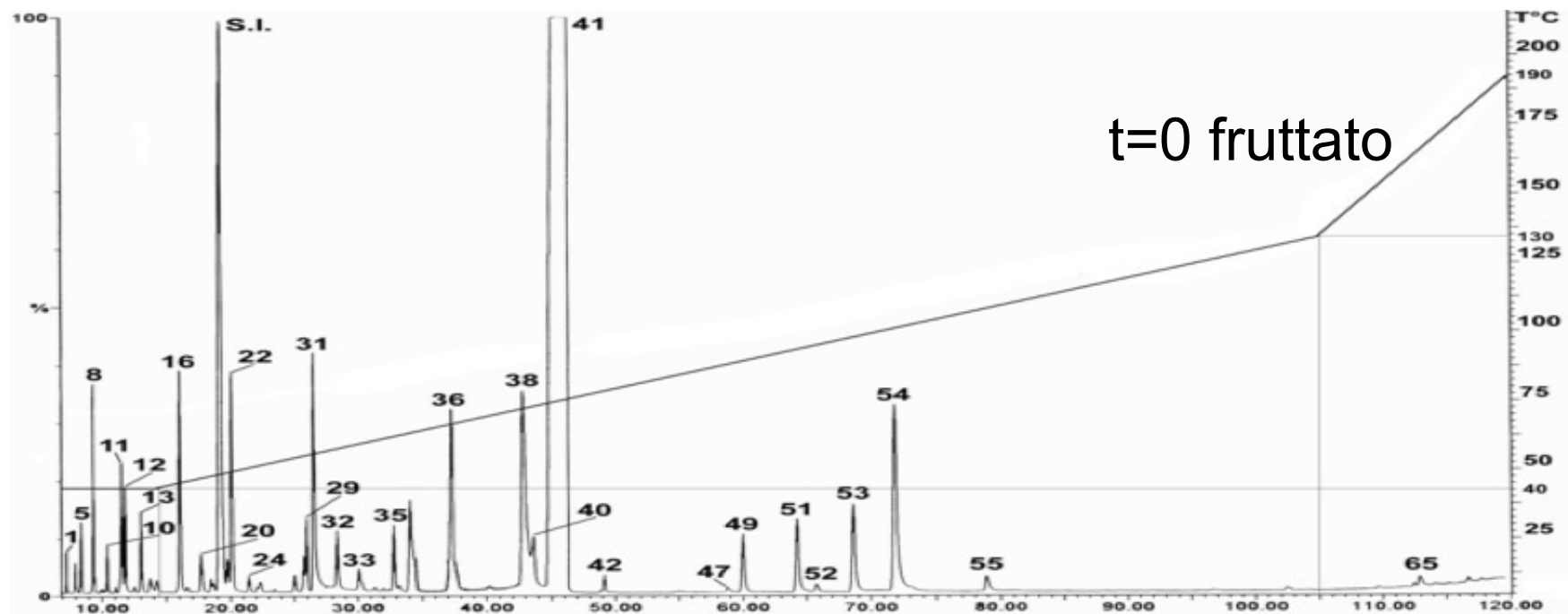
# **La biogenesi dei difetti ed il loro accertamento strumentale (GC/MS)**

2000-2017

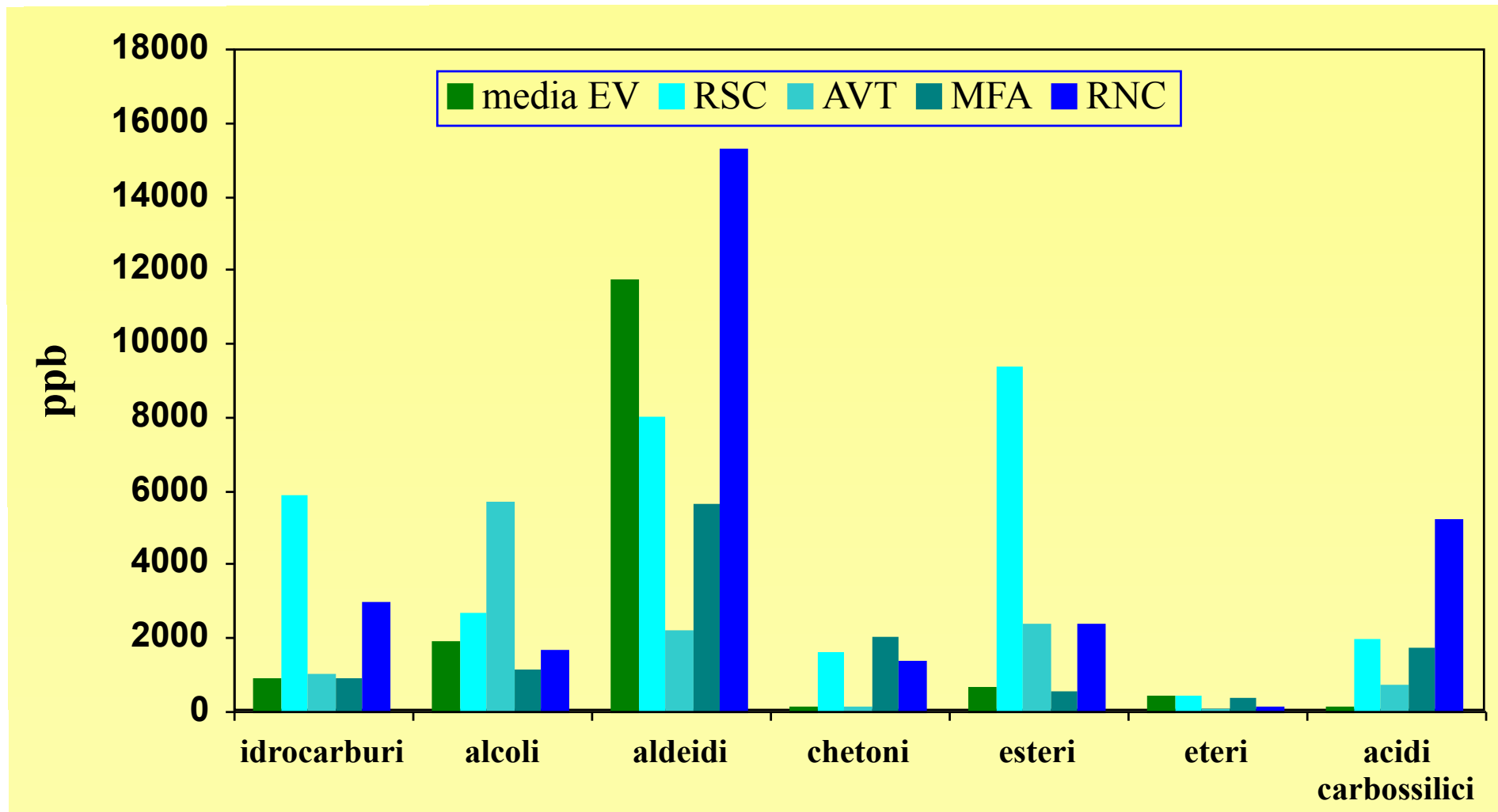
Esempio di profilo cromatografico GC/MS della corrente ionica totale (TIC) di un olio extra vergine di oliva





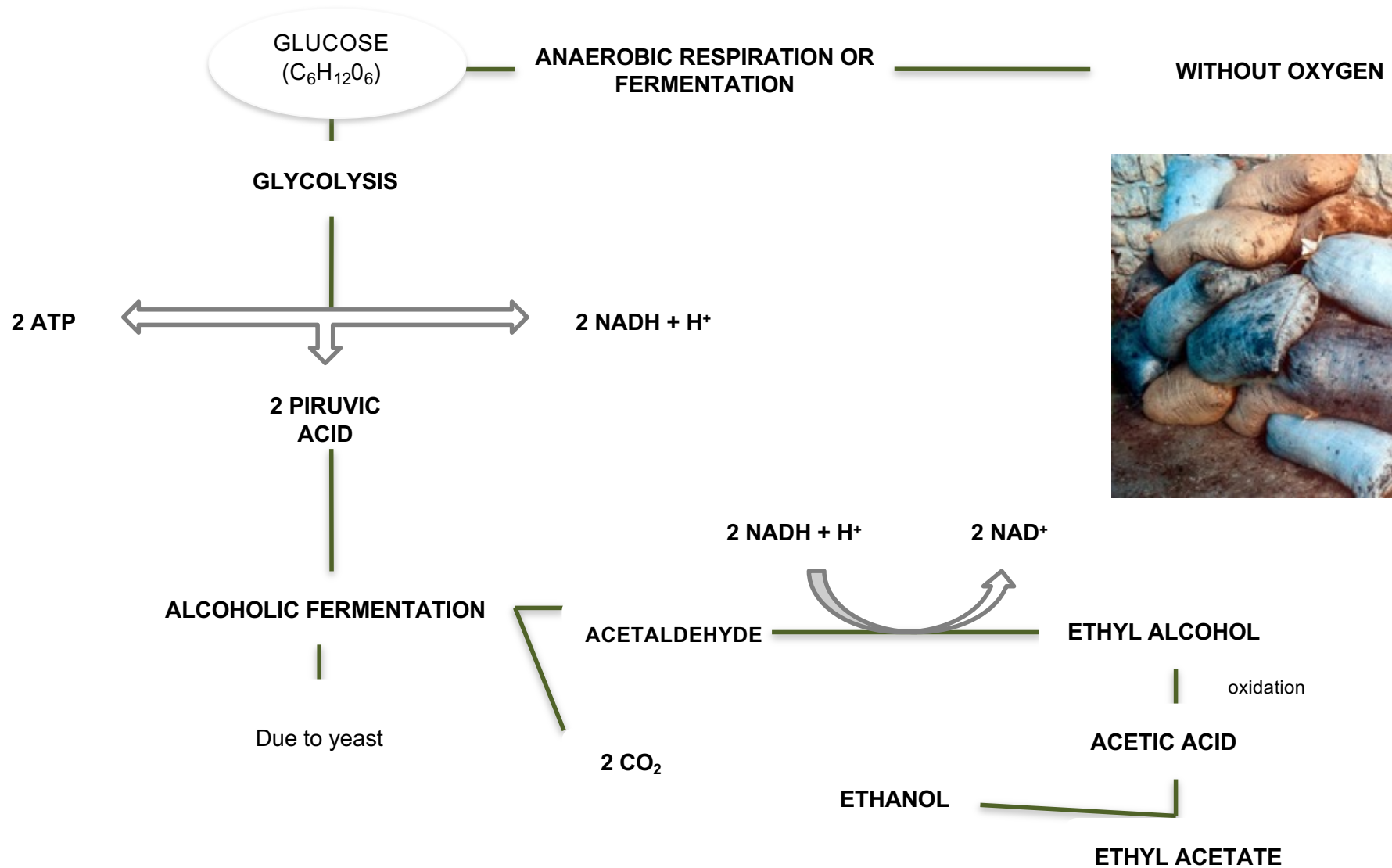


# Concentrazione delle classi di composti volatili

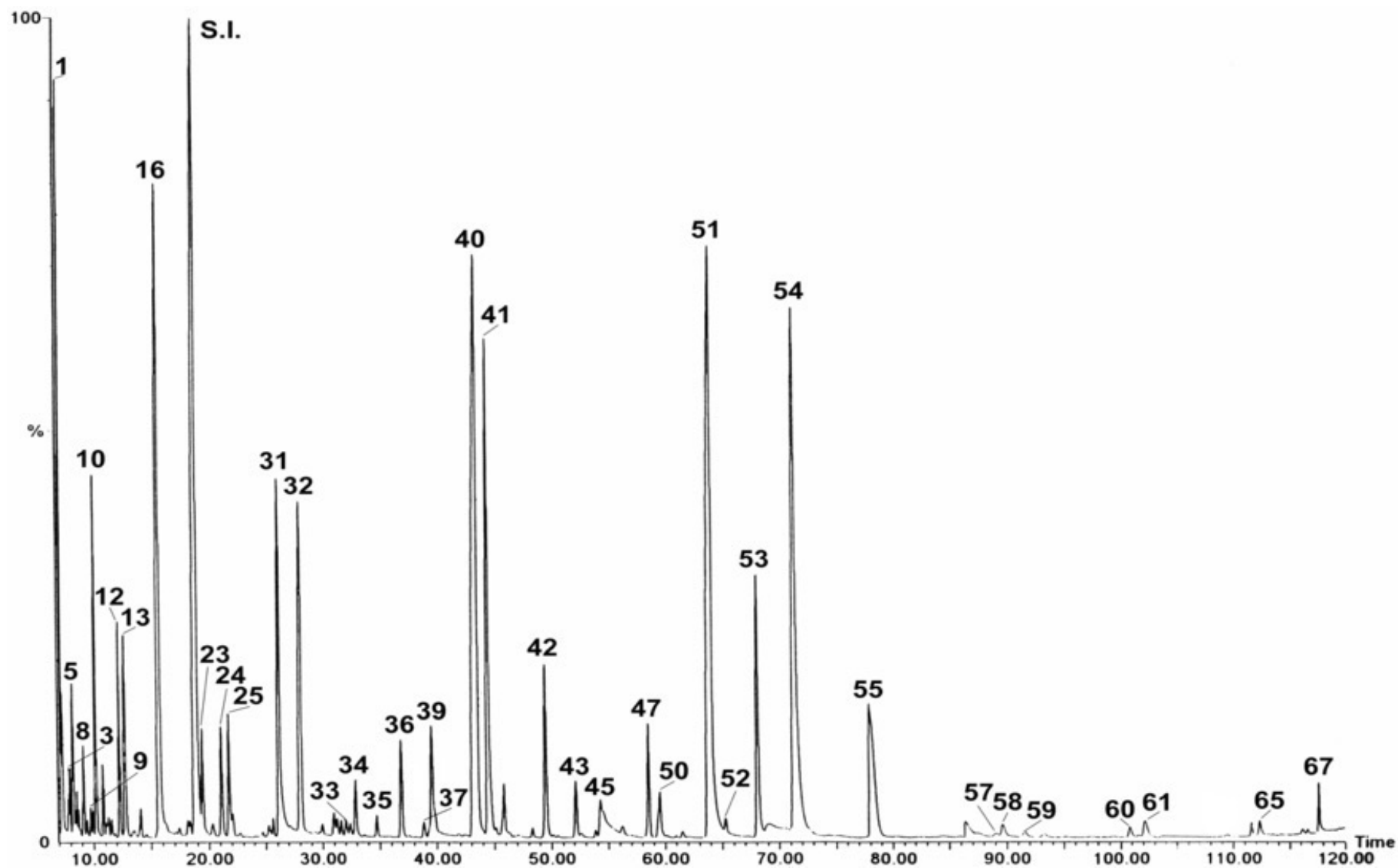


(Sacchi et al, 2000)

# AVVINATO-INACETITO ('WINEY')



# *Avvinato-inacetito*

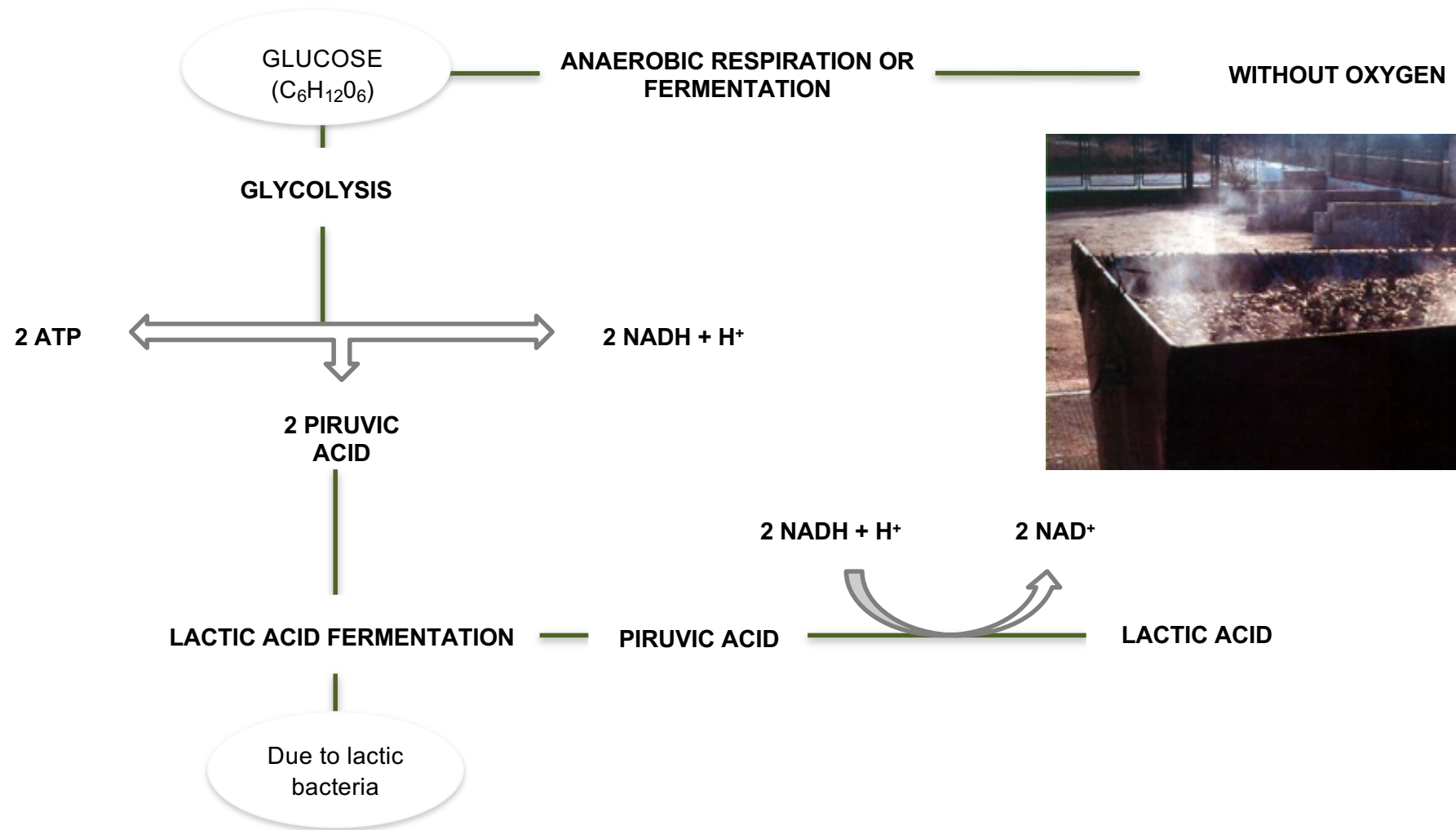




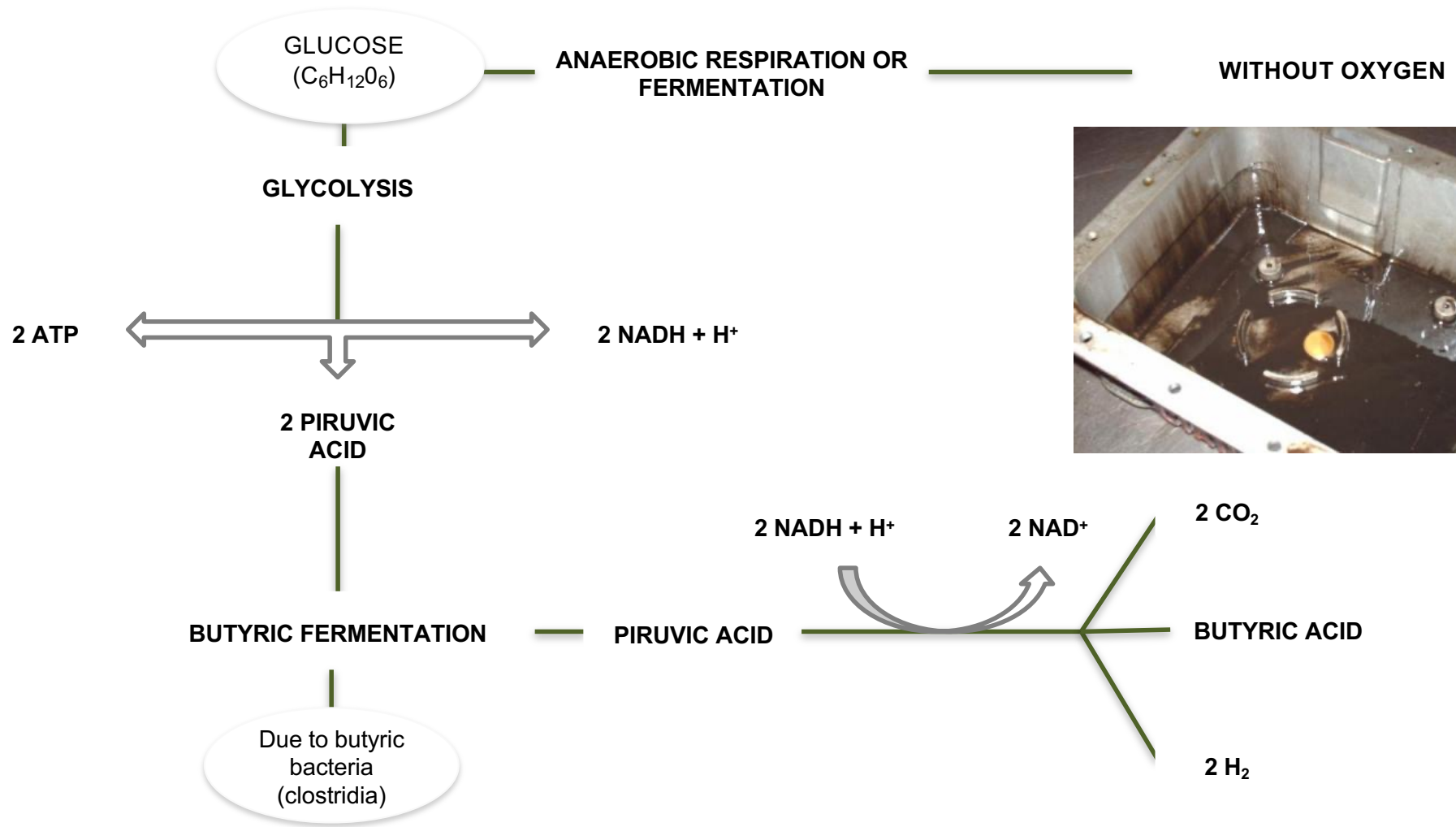
## *Avvinato-inacetito*

<b>Picco n°</b>	<b>COMPOSTO</b>	<b>Riferimento Bibliografico</b>
10	<b>etil acetato</b>	-
32	2-metil propanolo	Di giovacchino e Serraiocco, 1995
39	2-metil butanolo	Angerosa <i>et al</i> , 1995
40	3-metil butanolo	Di giovacchino e Serraiocco, 1995
51	esanolo	Angerosa <i>et al</i> , 1995
59	ottanolo	-

# RISCALDO ('FUSTY')

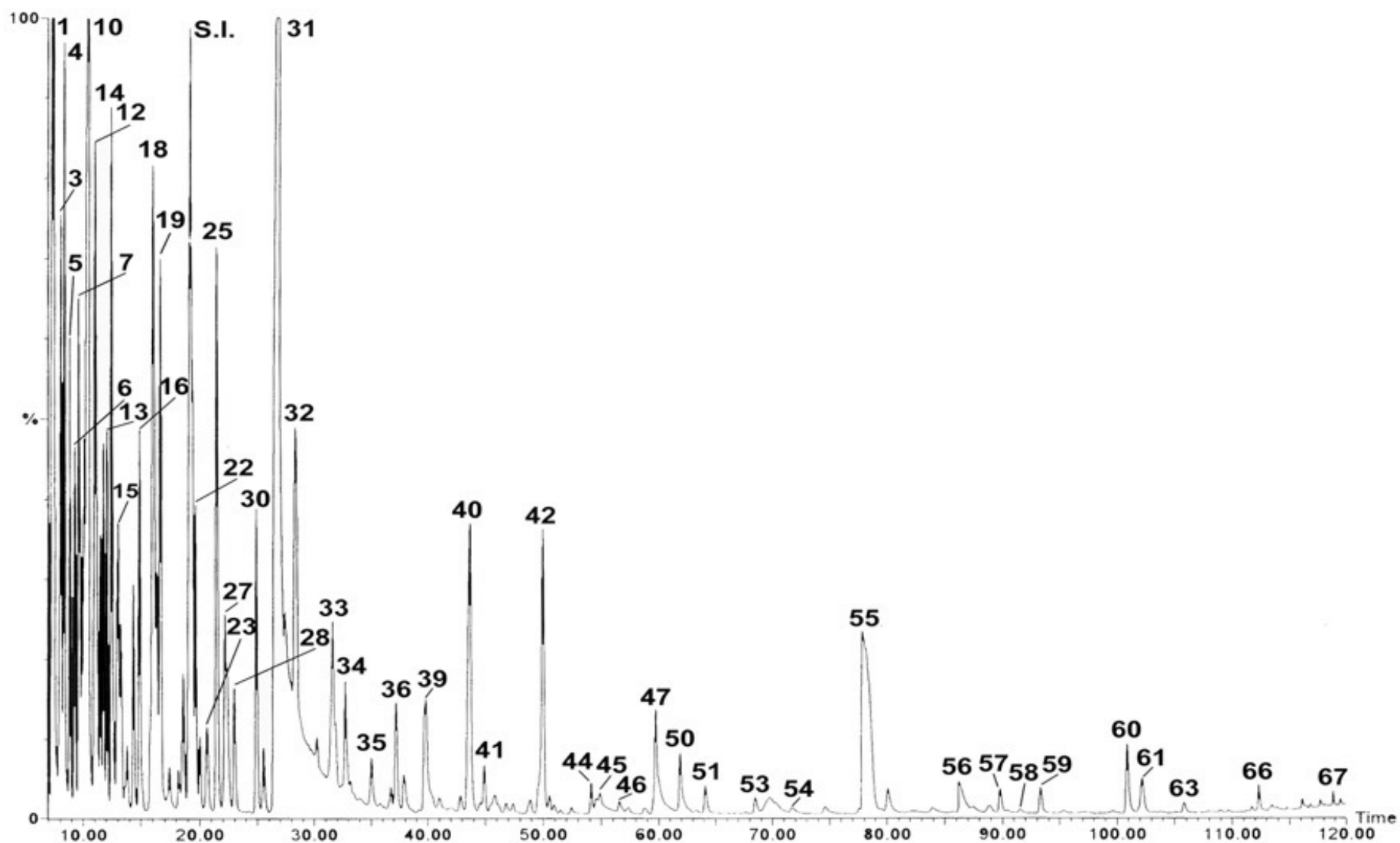


## 'MORCHIA' (MUDDY SEDIMENT)





# *Riscaldo*

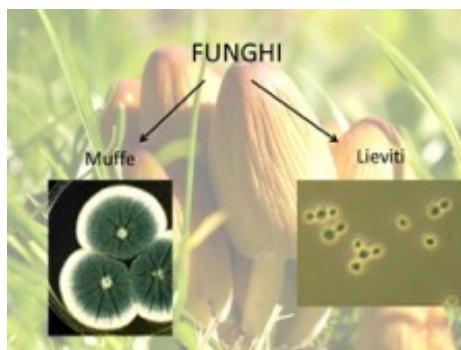


## *Riscaldo*

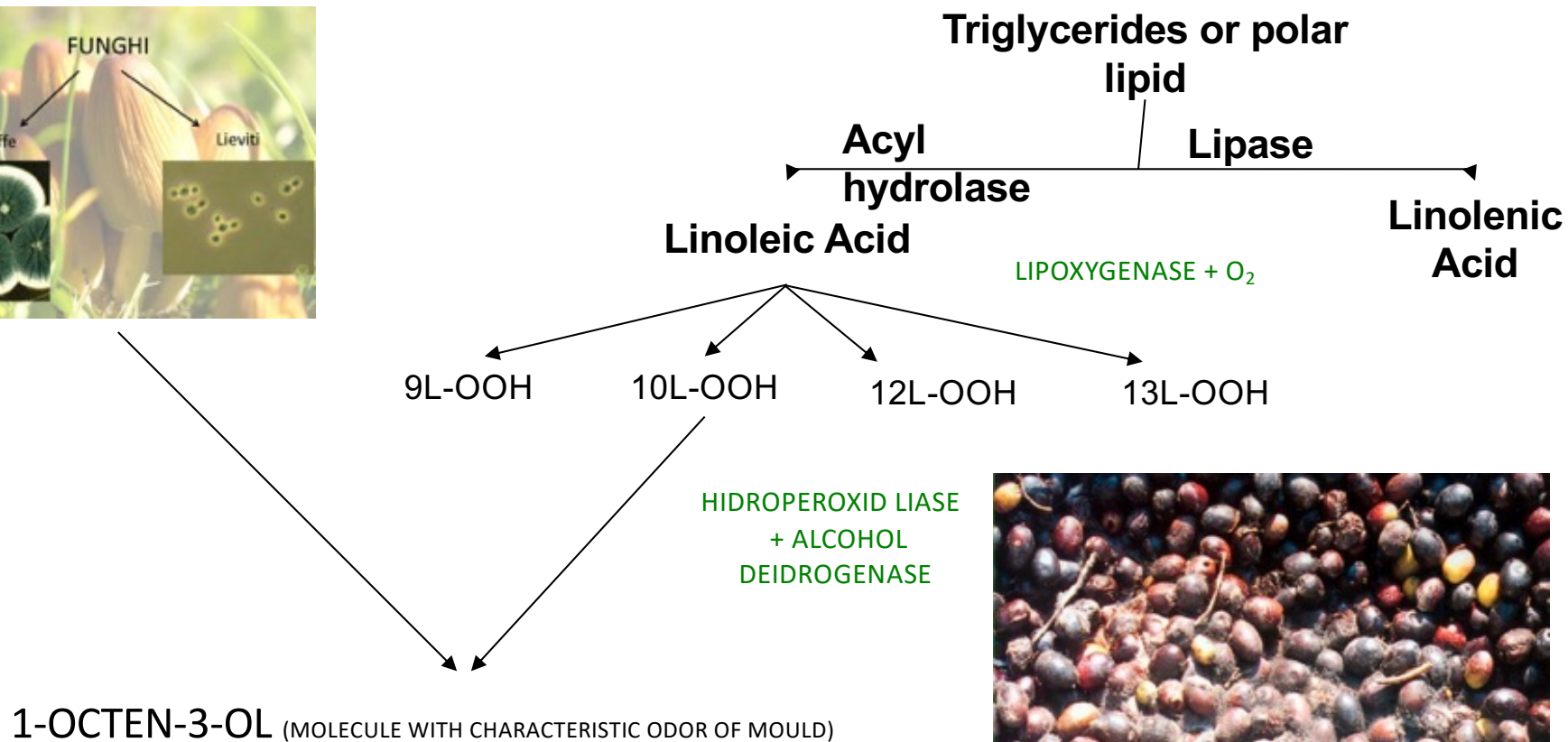
Picco n°	COMPOSTO	Riferimento Bibliografico
1	n-ottano	Di giovacchino e Serraiocco, 1995
3	2-metil propanale	Angerosa <i>et al</i> , 1995
4	acetone	-
5	metil acetato	-
6	ottene	Angerosa <i>et al</i> , 1995
7	2-ottene	-
10	etil acetato	Di giovacchino e Serraiocco, 1995
12	<b>2-metil butanale</b>	-
13	<b>3-metil butanale</b>	-
15	<b>etil isobutirrato</b>	-
18	decano	-
19	<b>metil butirrato</b>	-
23	2-butanolo	Angerosa <i>et al</i> , 1995
25	<b>etil butirrato</b>	-
33	pentil acetato	-
42	1-pentanololo	-
55	acido acetico	Di giovacchino e Serraiocco, 1995
60	<b>acido butirrico</b>	-
63	acido pentanoico	-
66	acetaldeide	Angerosa <i>et al</i> , 1995

# MUFFA ('MOULDY')

## PRESENCE OF FUNGI

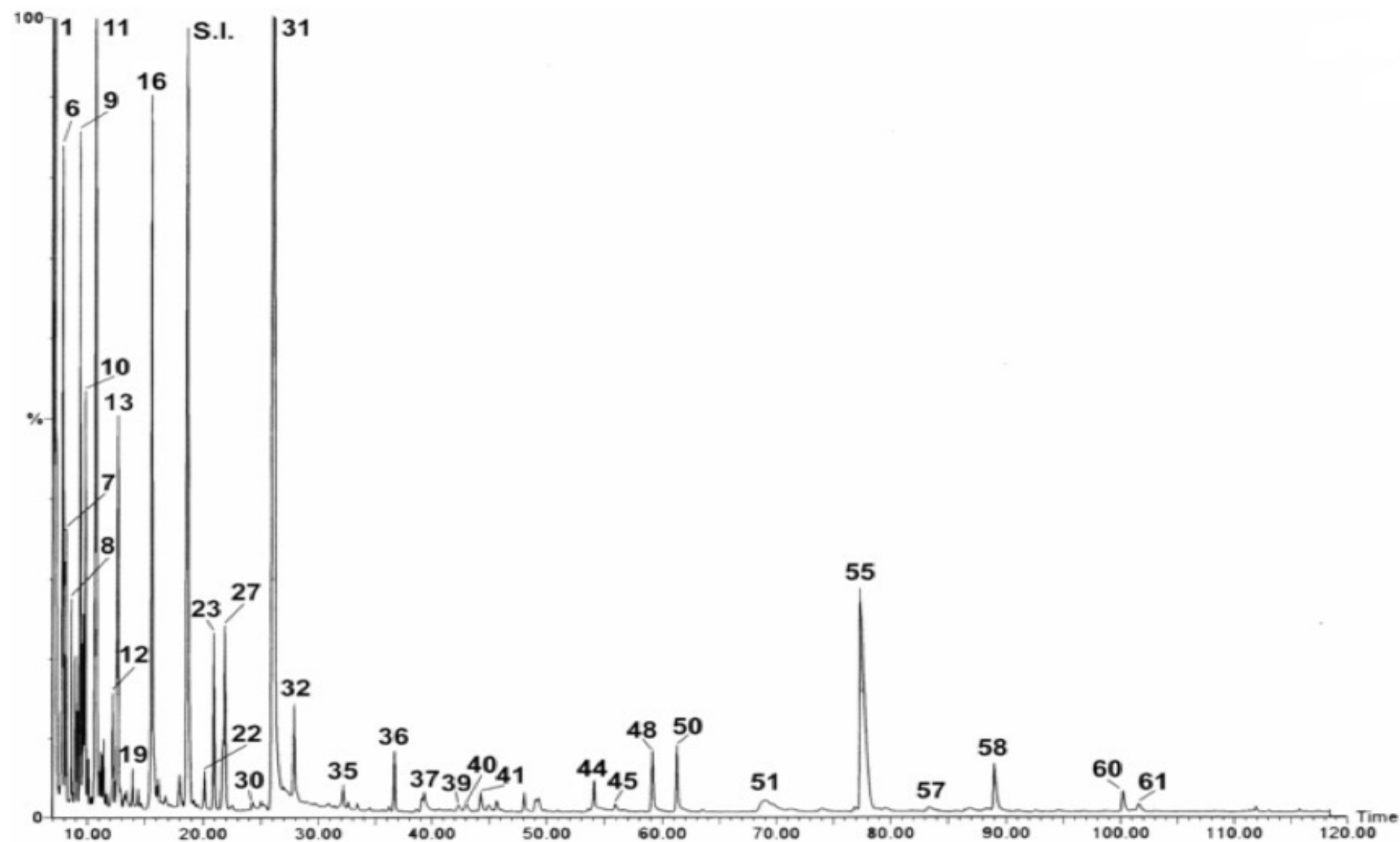


## PHOTOOXIDATION PROLONGED IN TIME





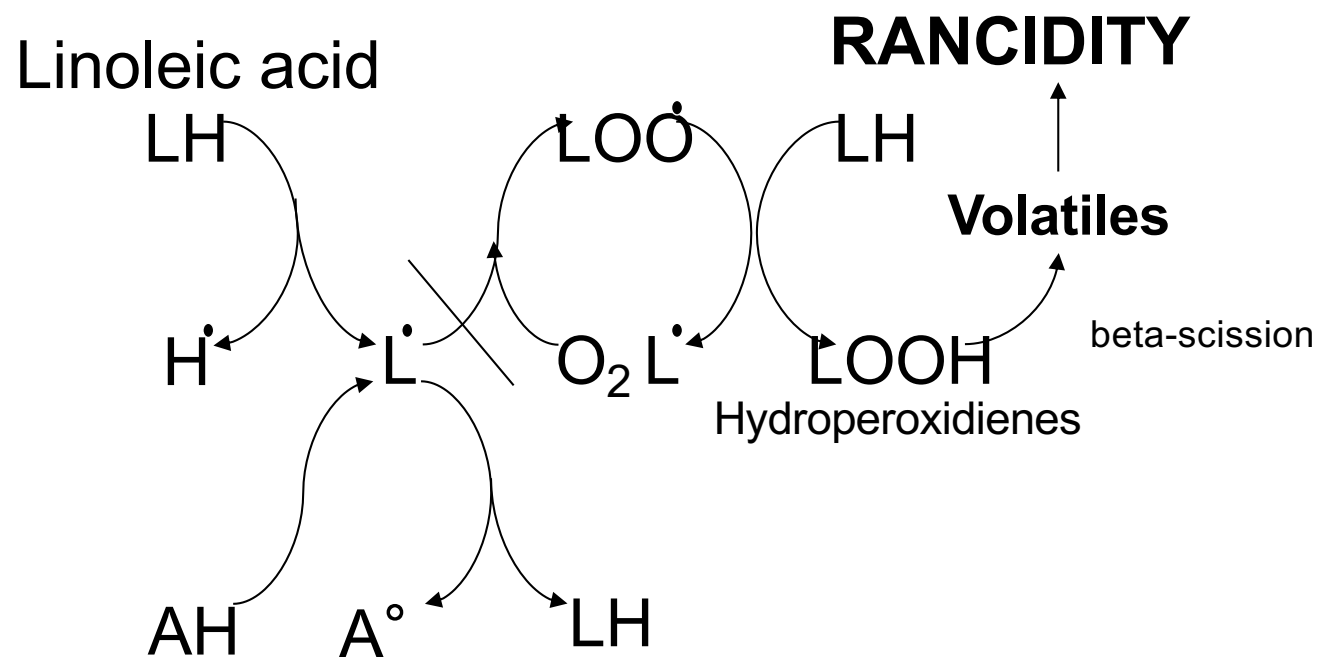
# *Muffa*



# Muffa

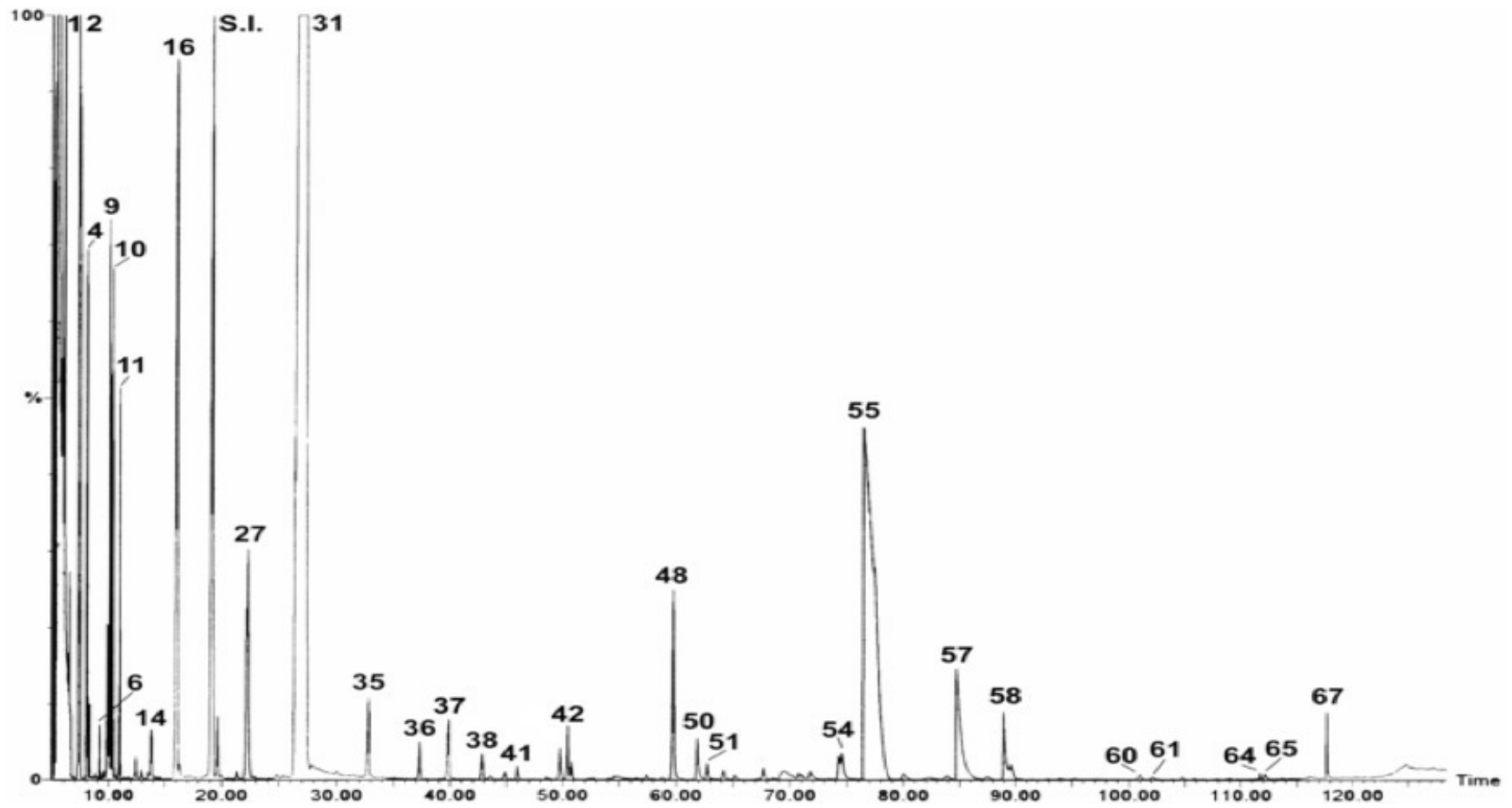
Picco n° Bibliografico	COMPOSTO	Riferimento
6	ottene	-
7	2-ottene	-
9	butanale	Angerosa <i>et al</i> , 1995
11	<b>2-butanone</b>	-
27	2-butenale	-
44	<b>2-ottanone</b>	-
50	<b>6-metil,5-epten,2-one</b>	-
55	acido acetico	Angerosa <i>et al</i> , 1995
58	<b>acido propionico</b>	-

## RANCIDO ('RANCID')





# *Rancido*



## *Rancido*

Picco n°	COMPOSTO	Riferimento Bibliografico
1	n-ottano	Di giovacchino e Serraiocco, 1995
2	nonano	-
16	1-pentenil acetato	-
31	<b>esanale</b>	Solinas et al,1987a
35	<b><i>trans</i>,2-pentenale</b>	-
37	<b>eptanale</b>	Solinas et al,1987a
48	<b>2-eptenale</b>	Solinas et al,1987a
55	acido acetico	-
57	<b><i>trans</i>,2-nonenale</b>	-
67	acido,2-metil pentanoico	-

## SPME-GC/MS Analysis of Volatiles

### Extraction of volatile compound by analysis of the dynamic head space(SPME):

-2g sample of oil in VIAL 20 mL +10  $\mu$ L of S.I.(Isobutyl Acetate) for 10min at 40° C

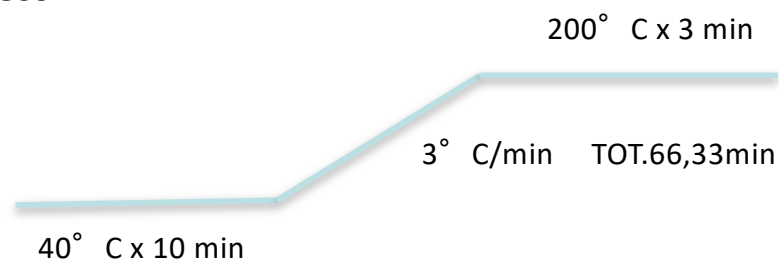
-the fiber is inserted (DVB/CAR/PDMS=grey 1cm) for adsorbiment of volatile compounds for 40 min at 40° C

(Romero et al.,2015)

### Analysis GC/MS:

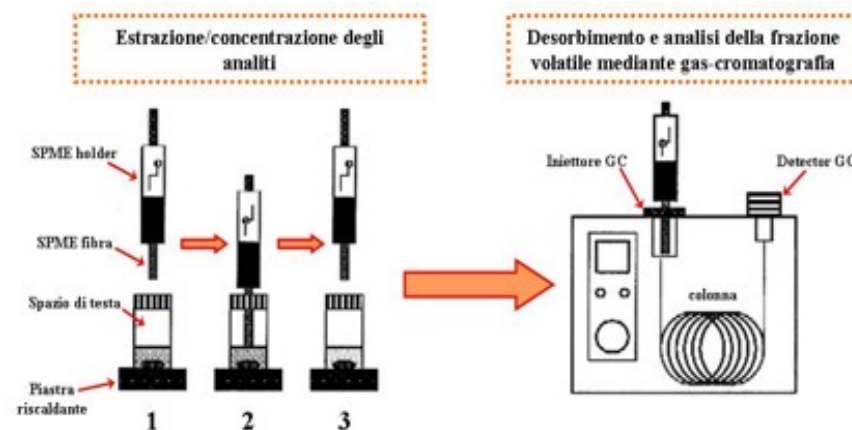
Flow= He 0.9 mL/min

Splitless



INJECTOR 300° C → 270° C  
GC/MS INTERFACE 280° C → 250° C  
MS SOURCE 180° C  
QUADRUPOLE 150° C  
MASS RANGE 40-300

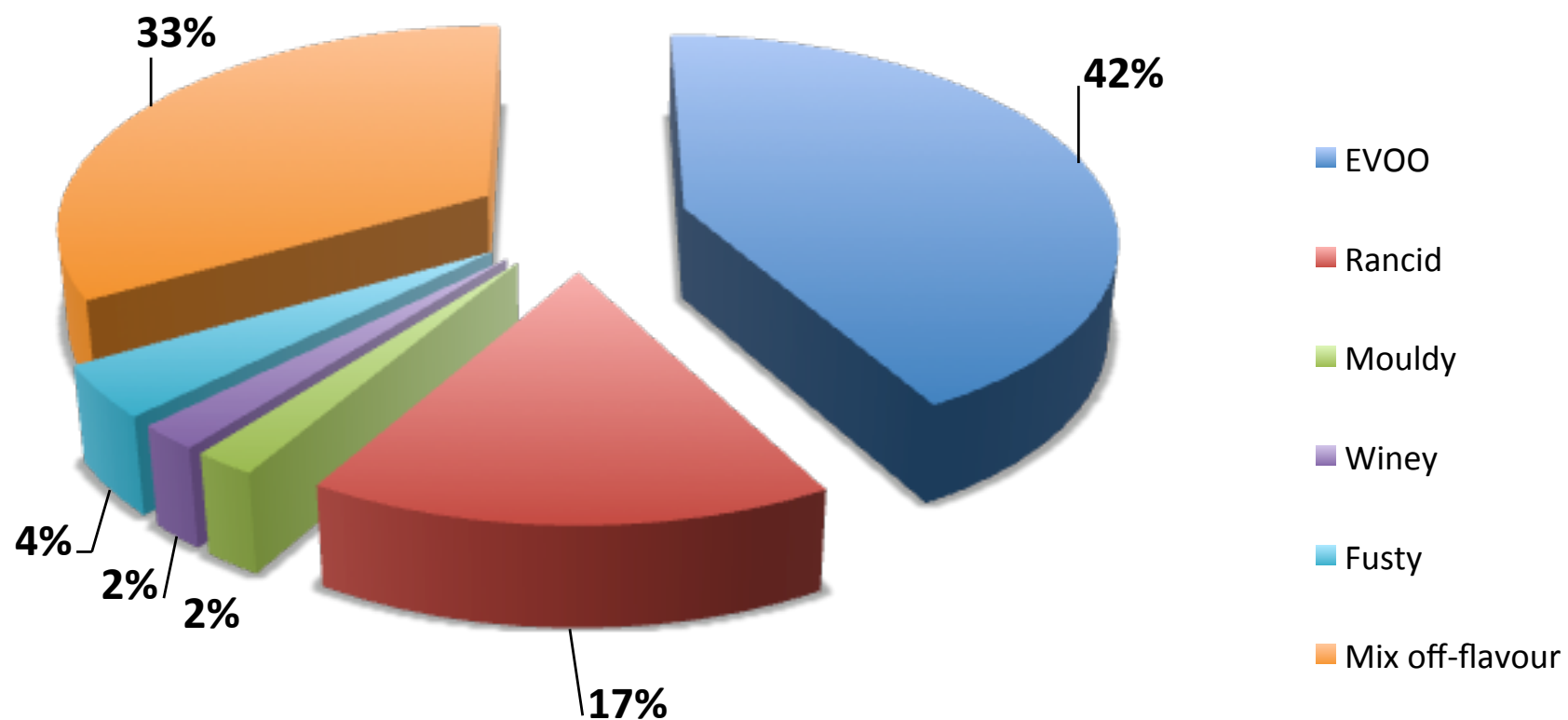
COLOMN:  
WAX 60m x 0.25mm  
0.25 $\mu$ m



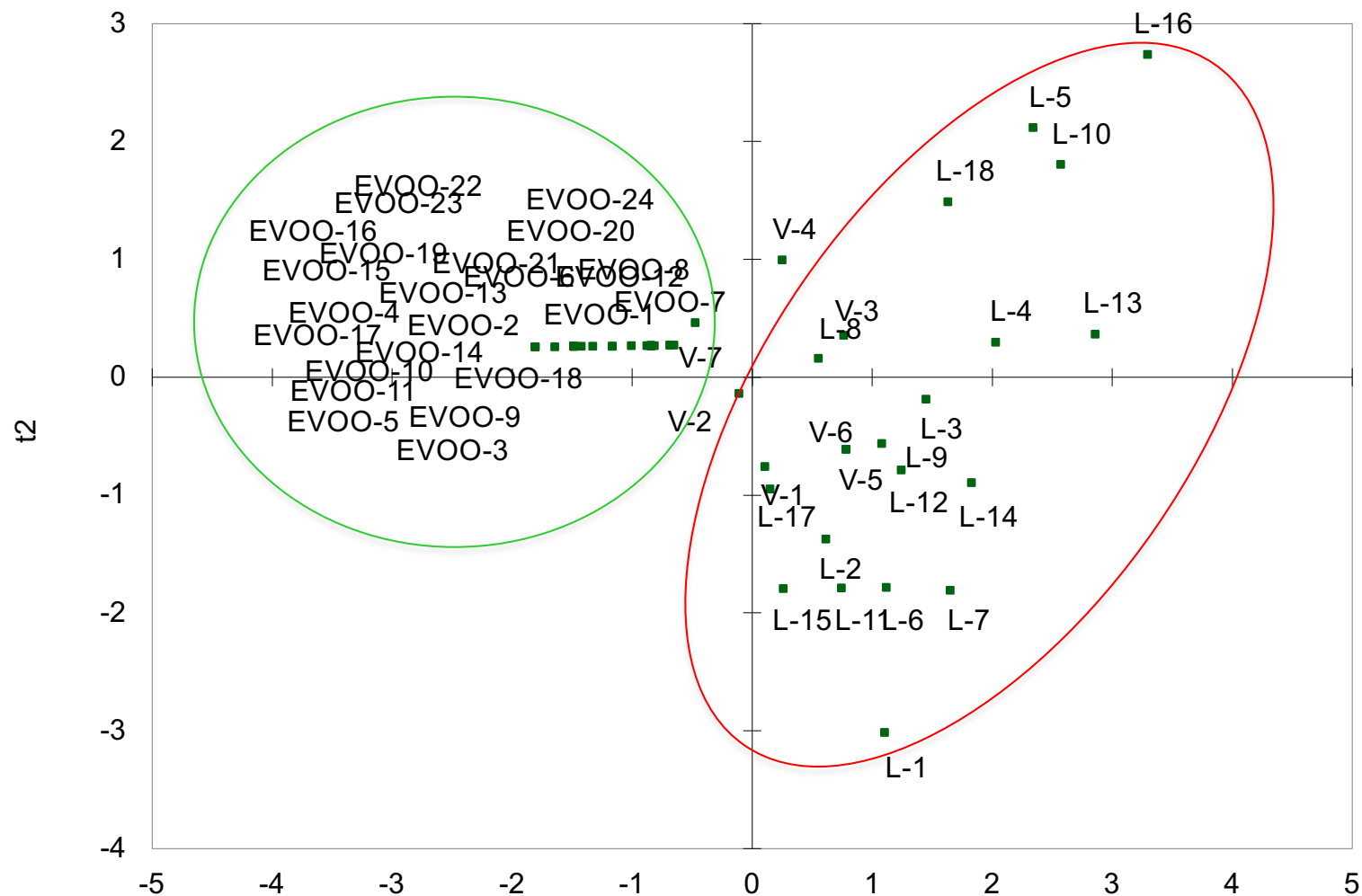
(Morales et al.,2005)



### Sensory properties of 49 olive oil samples used to validate the model

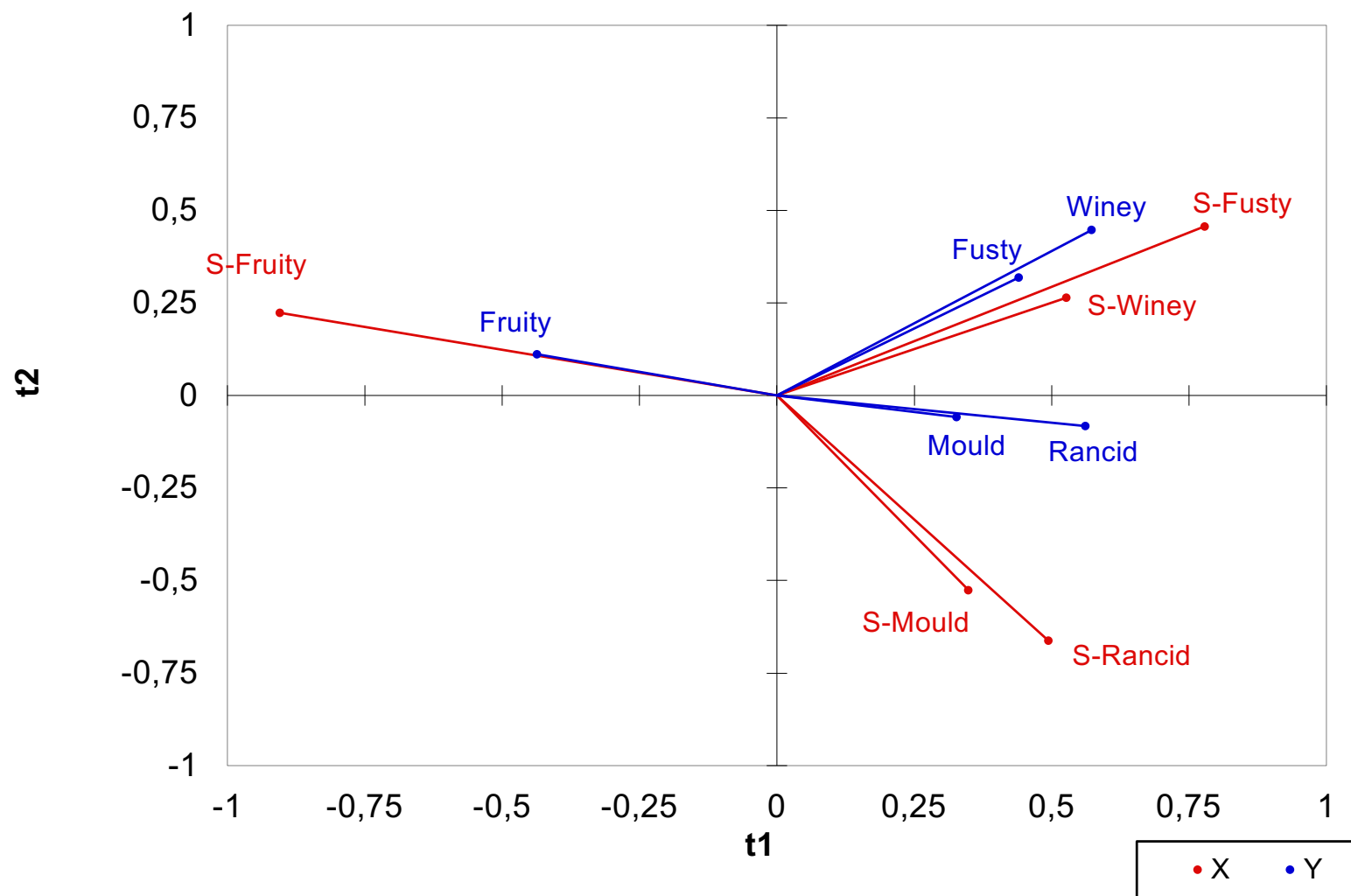


Osservazioni su assi t1 e t2



**PLS of aromatic series (X) vs sensory values (Y) (samples)**

### Correlazioni con t su assi t1 e t2



**PLS Analysis of aromatic series (X) vs sensory values (Y)**

## CONCLUSIONS

- The SPME-GC/MS analysis allows the determination of volatile compounds responsible for sensory defects (off-flavours) influencing the classification of olive oils.
- The method based on the Aromatic Series (OAV) should be applied to the quality control of commercial oils after further validation.
- The method could also become a key driver to confirm the response of *Panel test*, exceeding the low reproducibility of the sensory method and to make a prevision of defect perception during the shelf-life of 'border-line' extra virgin olive oils.