CHEMICAL ANALYSIS/ SENSORY ANALYSIS :

Molecular basis of wine aroma, quality and preference

LAAE
LABORATORIO DE ANÁLISIS DEL AROMA Y ENOLOGÍA

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UE FEDER
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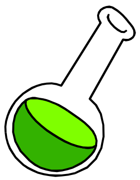
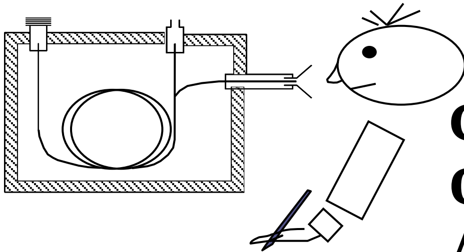
Aims of the talk

- To present the last advances in the understanding of the role played by wine aroma molecules on the sensory properties of wine
- These advances are mainly related to the way in which the different aroma molecules interact to form the different wine aroma nuances, in what we will call “the game of wine aroma”
- The basic elements of this game are:
  - The game field (the wine aromatic buffer)
  - The players (the odorants)
  - The roles and rules of the game

The work in a flash

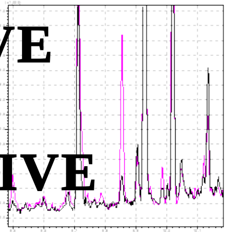


AROMA EXTRACTION



GC-OLFATOMETRY

GC-MS QUALITATIVE AND QUANTITATIVE

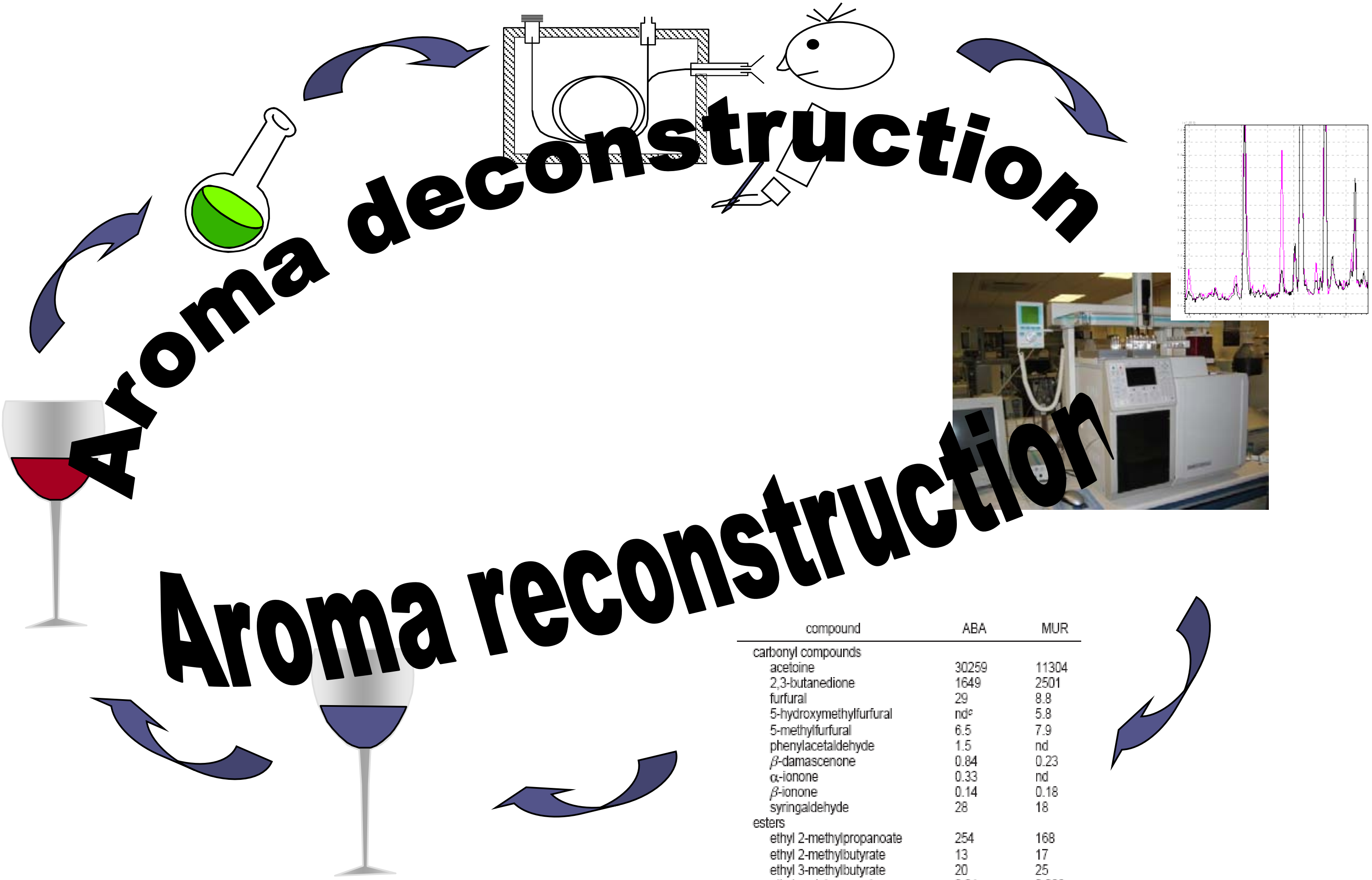


SENSORY TESTS OF RECONSTITUTION, OMISSION AND ADDITION

compound	ABA	MUR
carbonyl compounds		
acetoine	30259	11304
2,3-butanedione	1649	2501
furfural	29	8.8
5-hydroxymethylfurfural	nd[c]	5.8
5-methylfurfural	6.5	7.9
phenylacetaldehyde	1.5	nd
β-damascenone	0.84	0.23
α-ionone	0.33	nd
β-ionone	0.14	[illegible]
syringaldehyde	28	[illegible]
esters		
ethyl 2-methylpropanoate	254	[illegible]
ethyl 2-methylbutyrate	13	[illegible]
ethyl 3-methylbutyrate	20	25
ethyl cyclohexanoate	0.01	0.008
ethyl 2-methylpentanoate	0.012	[illegible]
ethyl 4-methylpentanoate	0.15	[illegible]
ethyl butyrate	170	75

EXHAUSTIVE QUANTITATIVE LISTS

The work in a flash



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β-ionone	0.14	0.18
syringaldehyde	28	18
esters		
ethyl 2-methylpropanoate	254	168
ethyl 2-methylbutyrate	13	17
ethyl 3-methylbutyrate	20	25
ethyl cyclohexanoate	0.01	0.008
ethyl 2-methylpentanoate	0.012	0.050
ethyl 4-methylpentanoate	0.15	0.10
ethyl butyrate	170	75

In short, what have we learnt?

1. Ethanol and the other major fermentation volatiles form an “aromatic buffer” which cannot be easily broken and which can have different degrees of strength
2. Only some selected molecules or group of molecules acting altogether (aroma vectors) can break effectively the buffer so that one of their own aroma nuances (primary or secondary) can be perceived above the aroma buffer
3. There are some molecules, that without being clearly perceived, cause a distortion and/or depreciation of wine aromatic quality and that must be considered as wine aroma defects
4. The most interesting and complex wines are those in which there are several aromatic vectors interacting well by simple addition, well by competition, well by hybridization to form a new aroma nuance

1. The aroma buffer caused by ethanol and the other wine major volatiles

(the playfield)

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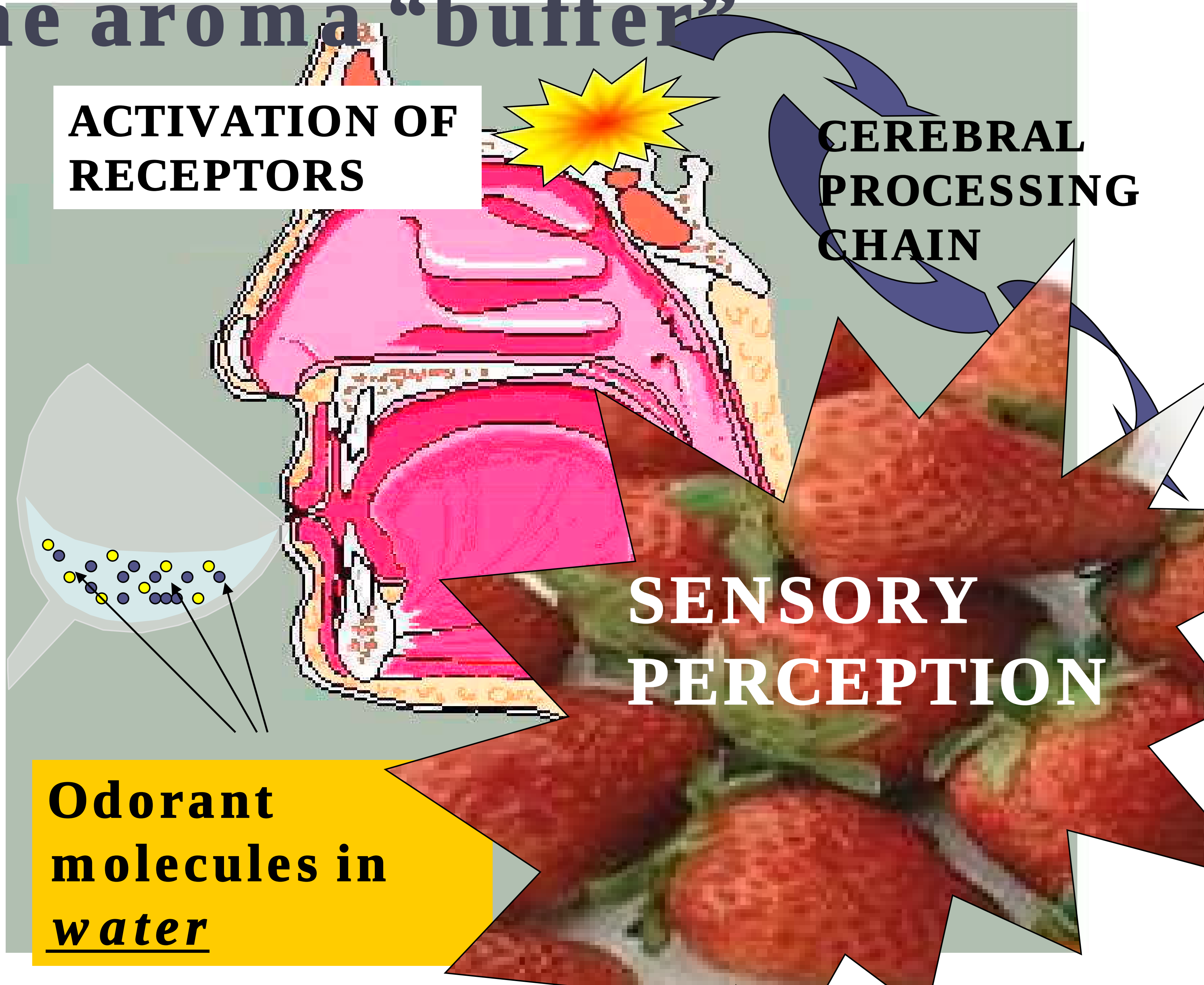
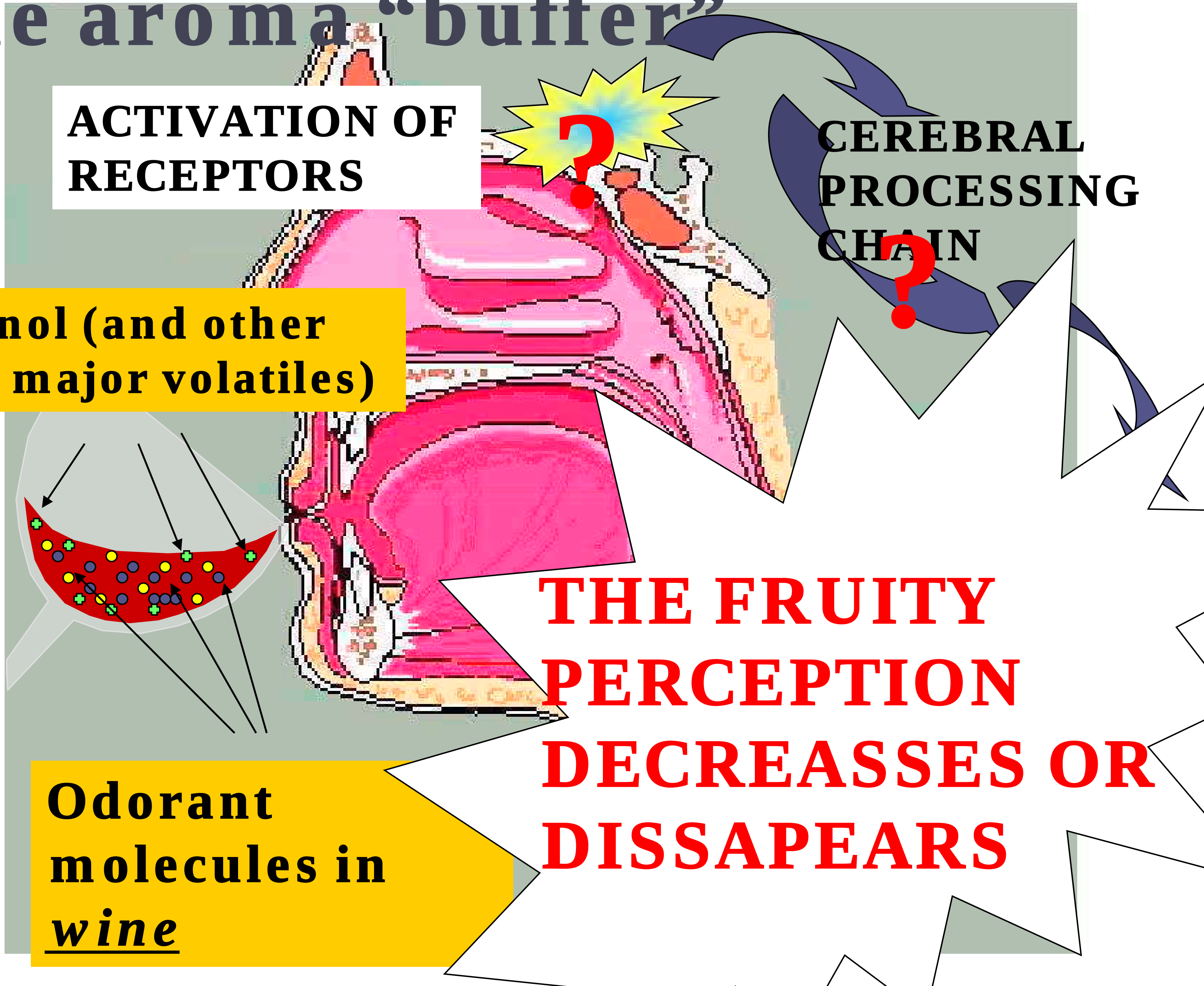
The base of wine aroma

- Formed by 27 chemical substances
- Present in all wines and naturally fermented alcoholic beverages
- At concentrations above the threshold
- Produce a typical vinous (sometimes just a plane or null aroma) aroma in which, most often, individual aroma nuances cannot be perceived
- They form what we will call an "AROMATIC BUFFER"

The aroma "buffer"



The aroma "buffer"



The buffering effect of the base

- The buffering effect causes that many changes in the aroma composition of the mixture have a null or very small sensory effect. When such effect is perceived, very often happens in an unexpected way
- Those effects are noted both when some constitutive components of the base mixture are removed or when some different aroma compounds are added on the mixture

The buffering effect of the base-1

Effect of omitting in the mixture:

isobutanol	NONE
Ethyl isovalerate	NONE
Ethyl 2-methylbutyrate	NONE
Ethyl isobutyrate	NONE
Ethyl butyrate	NONE
Ethyl acetate	NONE
Acetaldehyde	NONE
Diacetyl	NONE

In all cases concentrations were well above the odor thresholds

From Ferreira et al, J. Agric. Food Chem., 2002

The buffering effect of the base-2

Effect of omitting in the mixture:

Compound	Signif	Qualitative effect
β-phenylethanol	0.05	Negligible
Butyric acid	0.05	Negligible
Isoamyl alcohol	0.05	Negligible
E		Negligible
N		Negligible
C		
Hexano	0.05	
Ethyl ...noate	0.0	
Iso...aleric acid	...05	
Isoamyl acetate	0.05	Slightly less fruity
β-damascenone	0.05	Slightly less intense

This odorant seems to be an effective contributor to the fruity aroma

This odorant seems to exert an enhancing effect on aroma intensity

Tomado de Ferreira et al, J. Agric. Food Chem., 2002

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The buffering effect of the base-3

Effects of **adding** to the mixture:

Hexanoic acid(6.2 ppm; 2.5x)	Slight	- fruity; - sweet
β-phenylethanol (300 ppm; 21x)	NS	
Isoamyl acetate (5.5 ppm; 2.2x)	Slight	+ banana
Ethyl octanoate (6.0 ppm; 8.6x)	NS	
Sotolon (140 ppb; 2.8x)	Neat	- fruity; - sweet
β-damascenone (4.5 ppb; 1x)	NS	

Only in this case the sensory effect is clearly related to the aroma quality of the added odorant

Only this odorant has real power to break this particular buffer

Tomado de Escudero et al, J.Agric.Food Chem., 2004

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Are all buffers equally strong?

- **No; in general, the higher the level of alcohols, the more aggressive the buffer will be, and breaking it will be far more difficult**
- **Hence, the more difficult will be to have an aromatic perception clearly different to the "vinous" or "plane aroma"**
- **The role of the other major wine aroma volatiles is more complex and is yet under study**

2. Breaking the buffer:

A classification of wine aroma compounds (the players)

How can the buffer be broken?

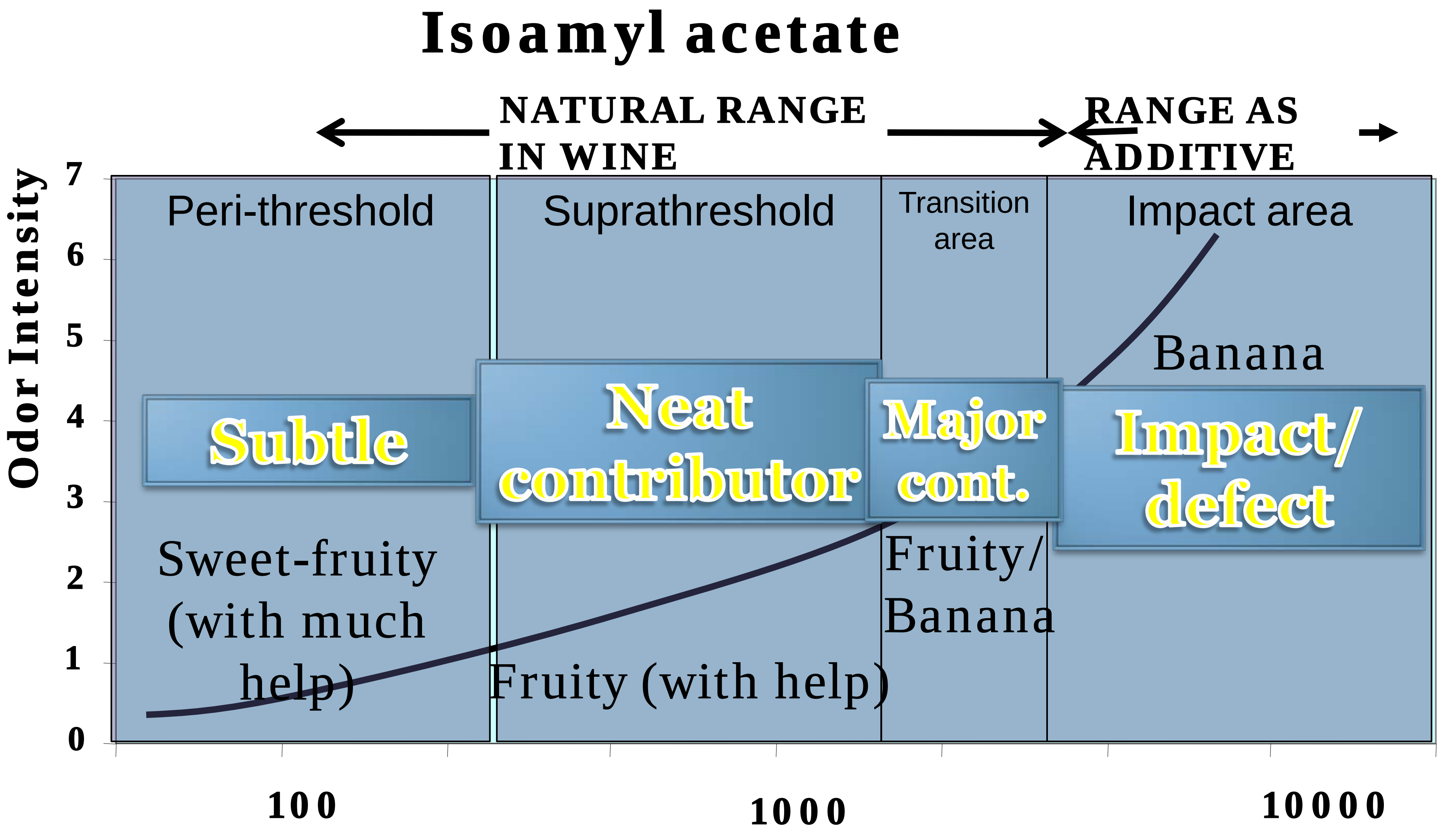
- **By a single odorant molecule at concentration large enough**
- **By a chemical and aromatic homologous group of aroma molecules**
- **By a combination of several groups of molecules sharing some aromatic descriptor**

Impact odorants

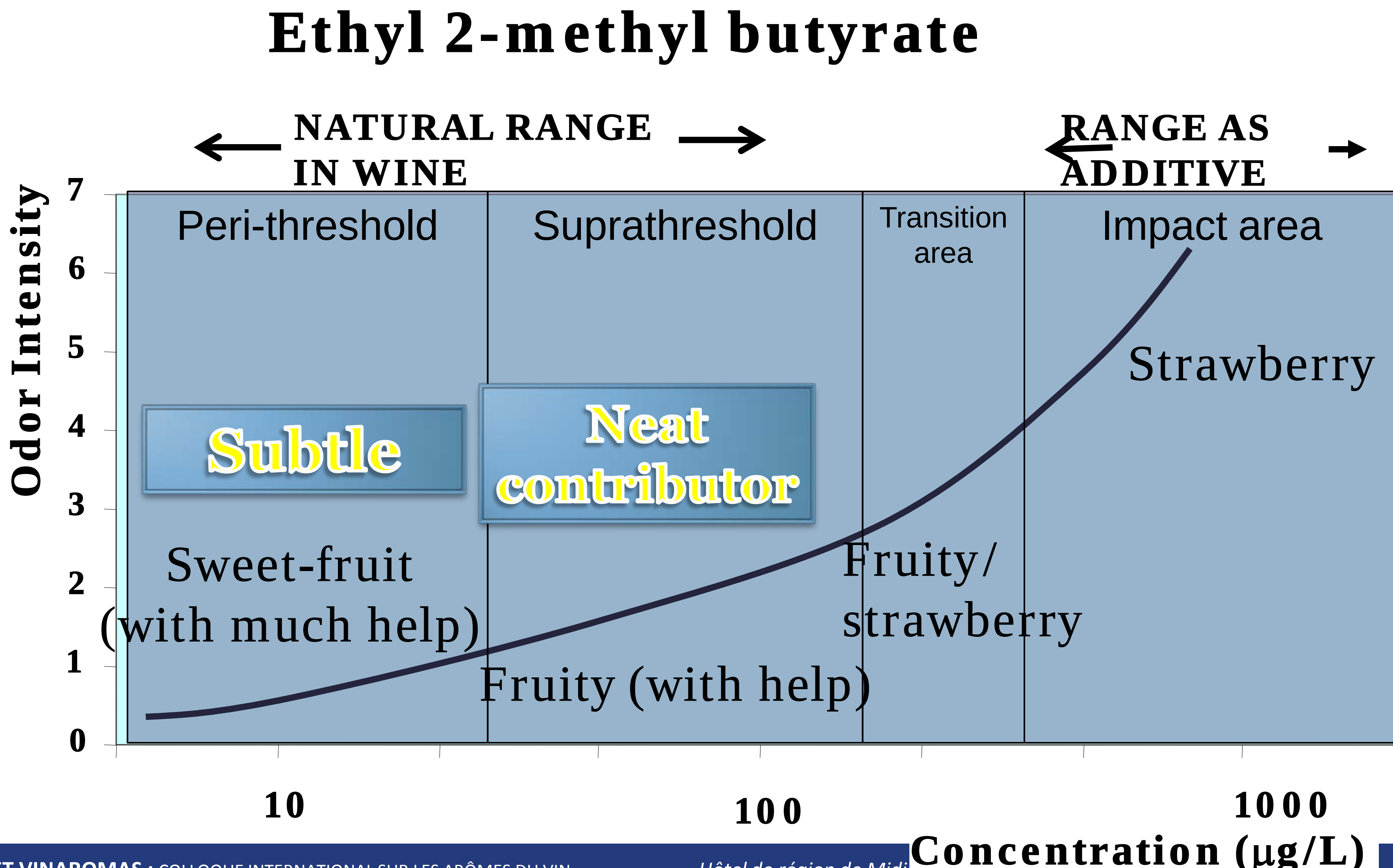
Impact families

Subtle or minor aroma compounds/families

Sensory effect and concentration



Sensory effect and concentration



A classification of wine odorants

(as a function of their potential role)

1. **Impact compounds or families**

CAN transmit its (their) specific or characteristic aroma to some wines. Its (their) omission cause a radical change on wine aroma

2. **Major contributors**

CAN transmit a characteristic (not specific) aroma nuance to some wines. Its (their) omission will cause a strong quantitative effect and even a slight qualitative change

3. **Neat contributors**

CAN transmit only a generic part of its (their) aroma to the mixture. Its (their) omission will cause a decrease on aroma intensity, but not a qualitative change

4. **Minor contributors**

They contribute, together with many other components to a generic wine aroma nuance. Its omission can pass unnoticeable

Impact compounds

- Linalool, c-rose oxide & β-damascenone
- 4-Methyl-4-mercaptopentanone, 3-mercaptohexanol, 3-mercaptohexyl acetate
- Isoamyl acetate
- Whiskylactone
- Diacetyl
- Sotolon
- Methional, phenylacetad
- Dimethyl sulfide (ambigu
- Furfurylthiol and benzylmercaptane
- Rotundone

16 compounds which conform the 16 "primary colors" of wine aroma

Muscat p Gewurztraminer nd Pedro Ximenez (sun dried)

- Linalool, c-rose oxide & β-damascenone
- Sauv. blanc lethyl-4-mercaptopentanone, 3-
rcaptohexanol, 3-mercaptohexyl acetate
- Verdejo & S. blanc
- Some rosés, Sauternes amyl acetate
- Pinotage & Tempranillo
- Oaky w. Whiskylactone
- Diacetyl
- Some Chardon -nays
- Sotolon Jérez, PX, Oporto, VDN, Sauternes
- Methional, phenylacetadelhy Sauternes uous role)
- Dimethyl sulfide (ambiguous ro Chat. Du Pape
- Furfurylthiol and benzylmerc
- Some old wines
- Rotundo Some Australian Shyraz

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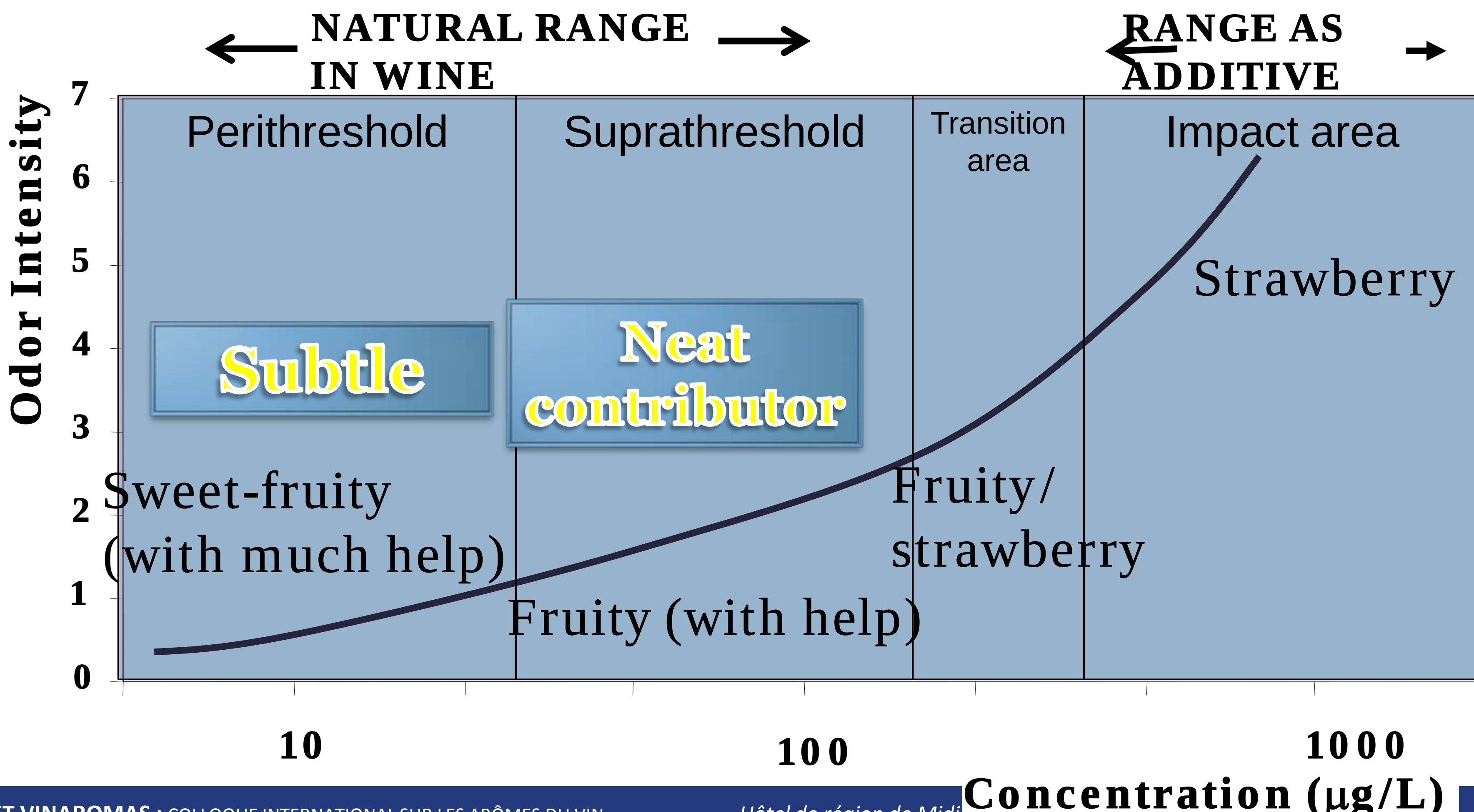
Aroma families

- Wine contains several groups of compounds that are formed through the same biosynthetic route, and that in addition can share the same aromatic and chemical properties
- These groups of compounds tend to act collectively exerting a concerted (additive) effect on wine aroma
- Example: ethyl esters of branched fatty acids
  - Ethyl 2-methylbutyrate, ethyl isobutyrate, ethyl isovalerate, ethyl 2,3 and 4-methylpentanoates

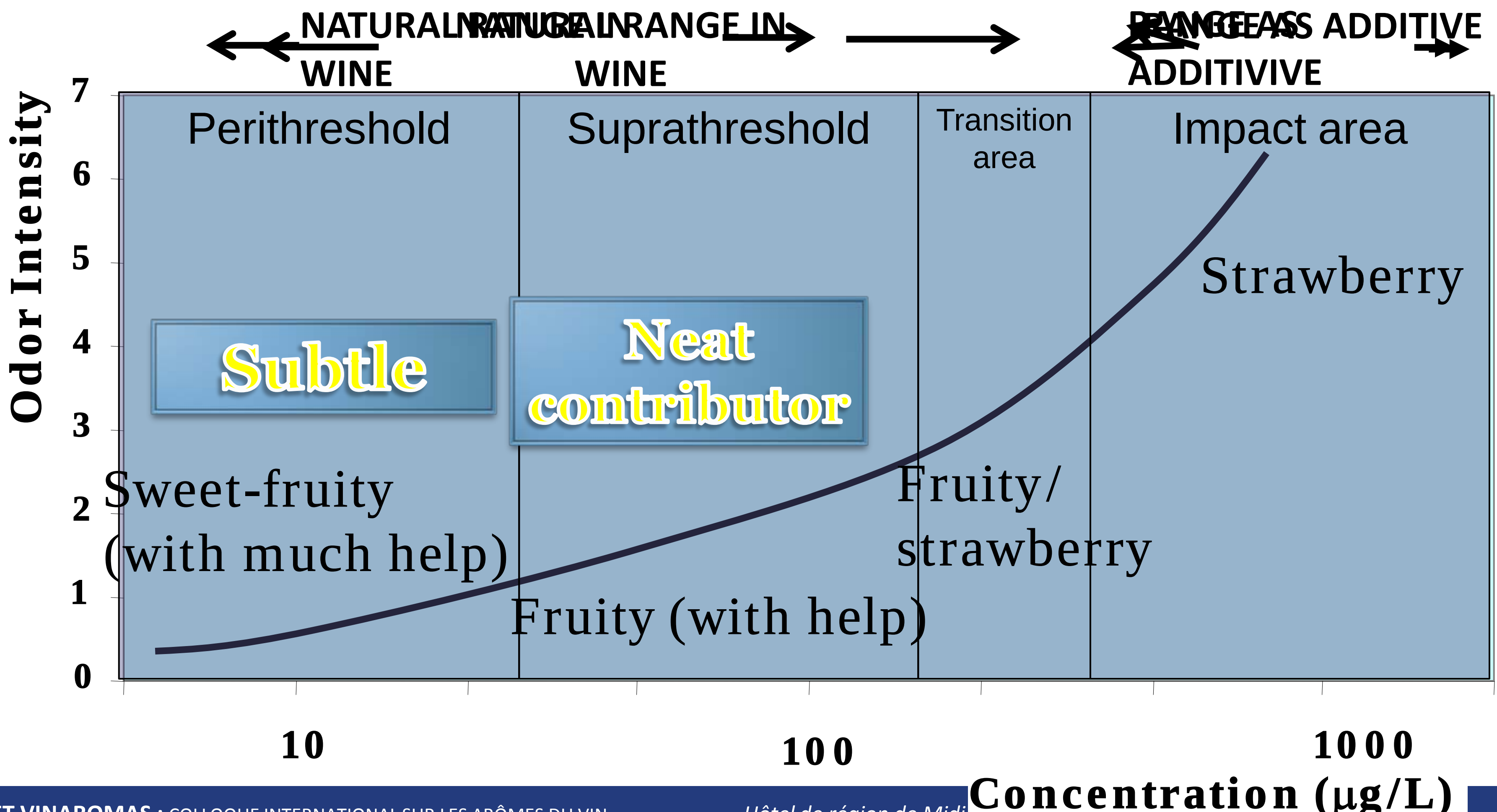
Aroma families

Ethyl 2-methyl butyrate



Aroma families

Family: ethyl esters of branched fatty acids (ethyl 2-methylbutyrate, ethyl isovalerate, ethyl isobutyrate...)



Other important families

- Vanillins: vanillin, ethyl vanillate, methyl vanillate, acetovanillone, syringaldehyde
- Burnt sugars: furaneol, maltol, homofuraneol, sotolon
- Volatile phenols: guaiacol, eugenol, isoeugenol, 2,6-dimetoxifenol, 4-alil-2,6-dimetoxifenol
- Etil cin
- Isoalde
  isovale
- Aldehí
- Ésteres etílicos de ácidos grasos
- Acetatos de los alcoholes de Fusel
- γ-lactonas alifáticas

Families add 10 more aromatic notes to wine (what for a painter would be 10 more colors in his palette)

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Aroma enhancers

- They are compounds that counteract the buffering suppression effect caused by ethanol and the other compounds in the base, making therefore possible that "hidden or buffered" aroma nuances become noticeable
- In some cases a new aromatic concept is formed. This effect seems to be strongly dependent on the enhancer concentration
- At least 3 molecules play such a role: β-damascenone, DMS, furaneol

Fruity aroma enhancers

Mixture of 13 fruity esters

- In water → Intense apple odor
- In water/ethanol → Low intensity undefined fruit
  - With 0.8 ppb β-damascenone and 0.1 ppb β-ionone → **Berry fruit**
  - With 3 ppb β-damascenone and 0.6 ppb β-ionone → **Plum, raisin**
- In wine → **No changes**
  - With 0.8 ppb β-damascenone and 0.1 ppb β-ionone / With 3 ppb β-damascenone and 0.6 ppb β-ionone → **No changes**
  - With 20 ppb DMS → **Berry fruit, cherry**

Escudero et al, J. Agric. Food Chem., 2007

Defects

Case of ethyl phenols

Case of rancios

Relative concept, extremely dependent on our experience and expectations

When it is not expected in the product

Case of sulfidric-rich wines

ase of wines with ethoxypyrazines

Only applicable when the off-odor is clearly perceived, when most often what is perceived is a vague absence of quality

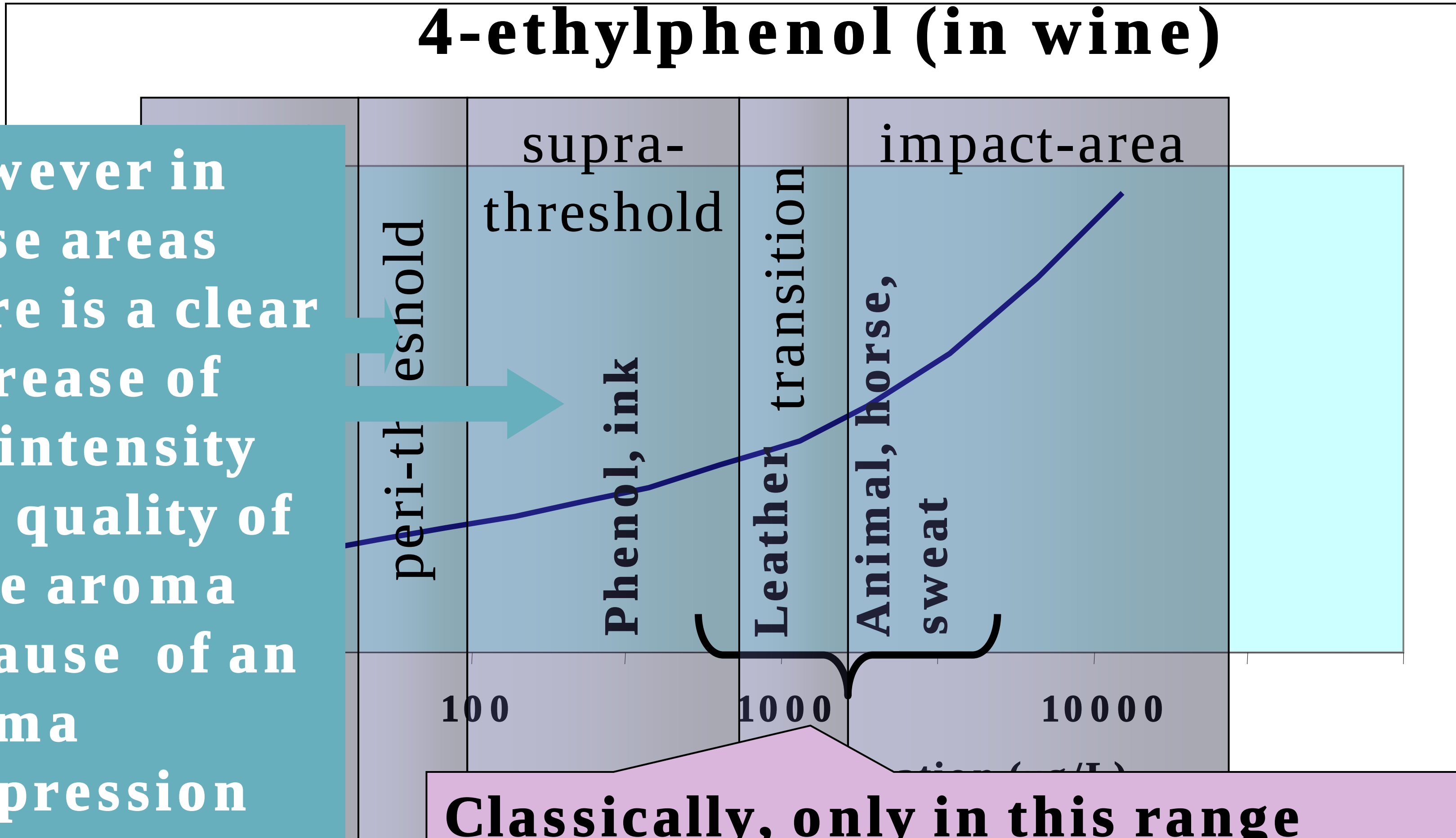
after its removal

Defects

This pragmatic definition has two advantages: Reduces the relativity Includes as defects all those substances that are really detrimental to wine aroma quality, even if they re not perceived. This is owadays the most requent case

When the aromatic quality of the product improves after its removal

Off-odors perception in complex mixtures



However in these areas there is a clear decrease of the intensity and quality of wine aroma because of an aroma suppression effect

Classically, only in this range ethylphenol is considered a problem

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Effects of 4-ethylphenol on wines of different fruitiness

RANKING TEST FOR FRUITY AROMA: Effect of the additions of 4-ethyl phenol on different wine models

	Level of 4-ethyl phenol (μg/L)				P(%)
	0	**50**	**120**	**700**	
fruit base 1 (without norisoprenoids)					
fruit base 2 (with norisoprenoids)					
fruit base 3 (base 2 + acids)					

Additions in all cases of just 50 ppb are perceived as less fruity, but the effects are evident only in wines with smaller fruity levels

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Defects

Attending to such definition, the following compounds can be considered quality depreciators:

- **Phenylacetaldeyde**
- **Ethyl phenols (4-ethyl phenol y 4-ethyl guaiacol)**
- **Methoxypyrazinas**
- **Acetic acid (también butírico e isobutírico)**
- **Acetoin**
- **Vinyl phenols (4-vinyl phenol and 4-vinyl guaiacol)**
- **TCA y TBA**
- **Mercaptanos**
- **E-2-alquenales**
- **Methional**
- **DMS**
- **TDN, TPB**
- **1-octen-3-ona**
- **Varias piridinas**

Sources (among others):
L. Culleré, PhD Thesis, Zaragoza 2005
E. Campo et al, J.Agric.Food Chem., 2005
Escudero et al, J.Agric.Food Chem., 2000
Chatonnet et al, J.Sci.Food Agric., 2002&2004
Sefton et al, J.Agric.Food Chem., 2005
...

Quality depreciators and quality

In **all** the models relating wine quality with composition ALWAYS we have observed a common structure:

QUALITY= Σpositive cont. – Σnegative cont.

Not being required that the negative contributors are above threshold!

Not being required that the wine show explicit problems either!

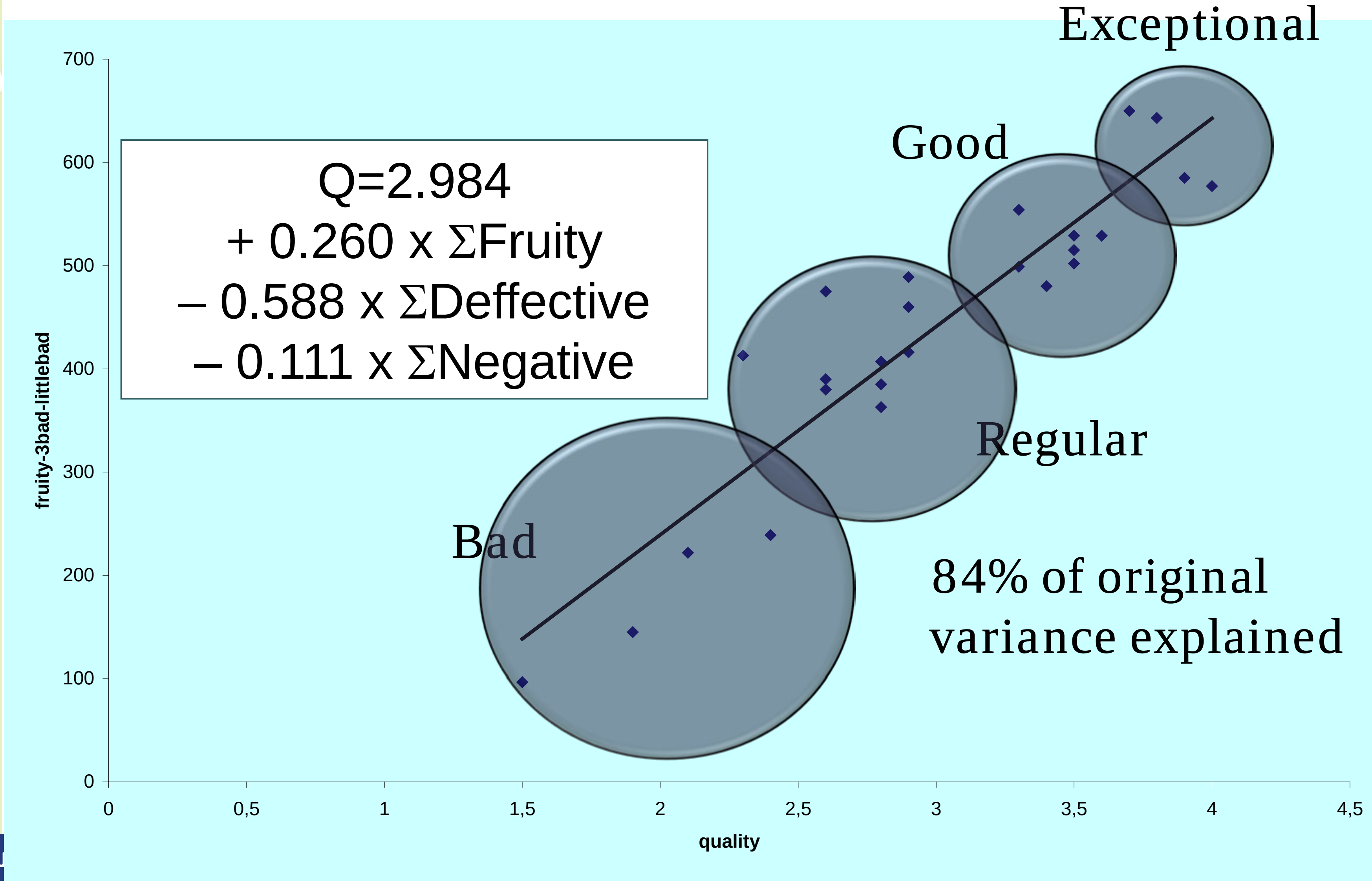
This fact, REPEATEDLY VERIFIED demonstrates the essential importance of quality depreciators on the perception of positive aroma nuances and on wine quality

Quality depreciators and wine quality: an example

MODELING QUALITY OF SPANISH PREMIUM RED WINES (J. Agric. Food Chem., 2009)
25 wines, quality assessed by 21 experts; A complete GC-Olfactometric profile was registered for each wine (65 odorants). Odorants were classified into 4 categories

- **Fruity:** 13 esters, β-damascenone and furaneol
- **Deffective:** TCA, 3,5-dimethyl-2-methoxipyrazine, 4-ethylphenol, 4-ethylguaiacol, 3-ethylphenol, o-cresol
- **Negative:** methionol, methional, c-2-nonenal, 1-octen-3-one, 2,4-decadienal, 2-methylbutanal, acetic acid, isopropil-2-methoxypyrazina, 2-methylisoborneol
- **Irrelevant** for the model: all the other odorants

A model for quality



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In summary

1. **27 aroma compounds form the base of the wine aroma perception (the aroma buffer). The strenght of the buffer is determined by their relative levels**
2. **47 aroma compounds (with 26 different aromatic nuances) are the main responsible for sensory differences between wine types and varieties:**
   1. ***16 potential impact compounds***
   2. ***31 in families with 10 different odors***
3. **3 compounds can act as aroma enhancers**
4. **More than 30 compounds can ruin quality (even if they cannot be noticed)**

3. The aromas of wines

Some examples of the game showing the players and the game rules

Floral note(white wines) and complexity

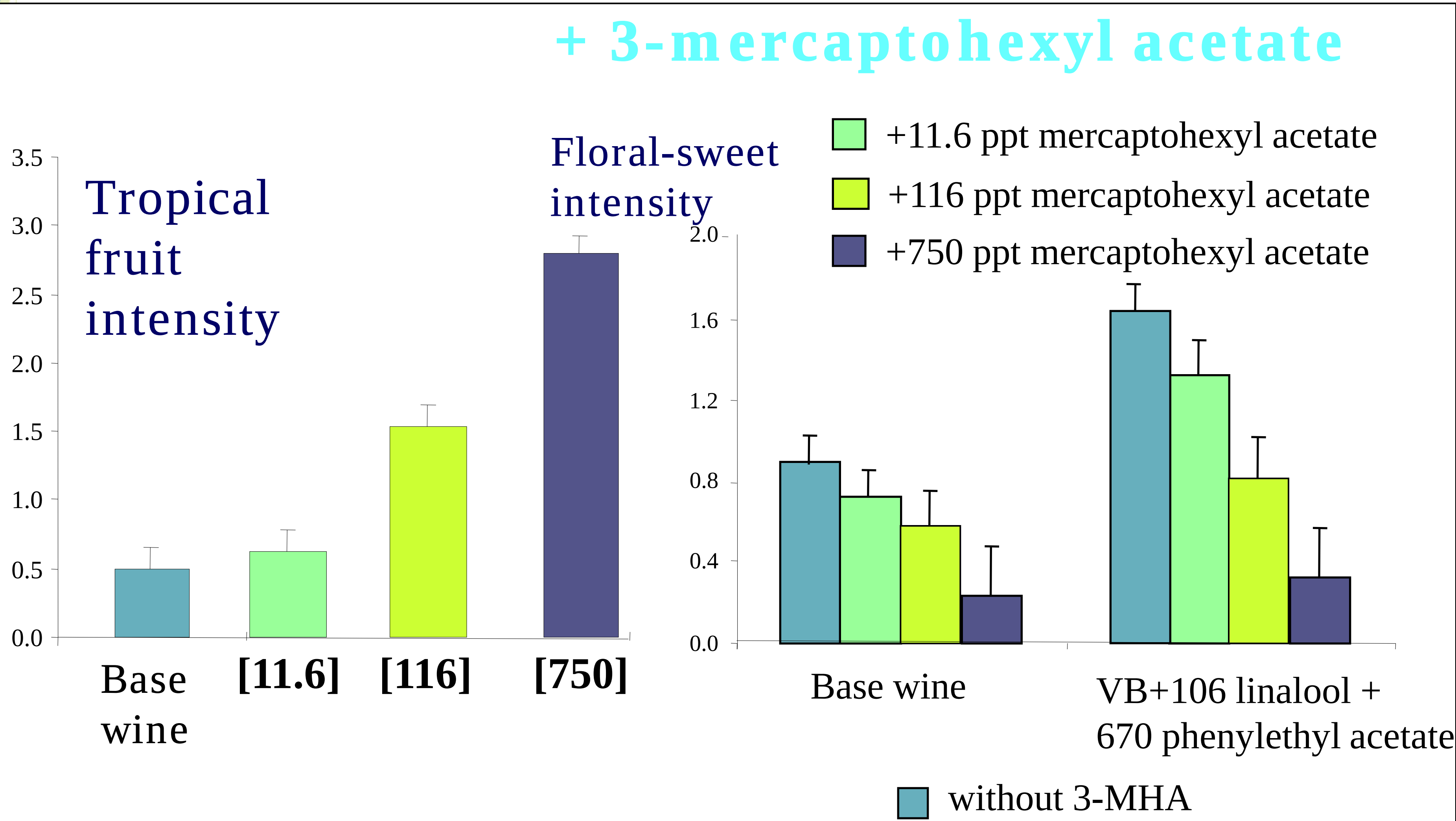
← **More simple** | **More complex** →

RULE OF COMPLEXITY: nearly always the products showing most complex and less explicit aroma are preferred

Muscat	Floral-Muscat	Floral-Sweet	Sweet-floral
Linalool and geraniol (>200 ppb)	linalool , geraniol α-terpineol nerol (>50 ppb)	Terpenols (>20 ppb) Ethyl cinnamates β-phenylethyl acetate	terpenols Ethyl cinnamates β-phenylethyl acetate vainillins γ-lactones

Interactions of flowery notes

Interactions of flowery notes



Campo et al, J. Agric. Food Chem., 2005

Interactions of flowery notes

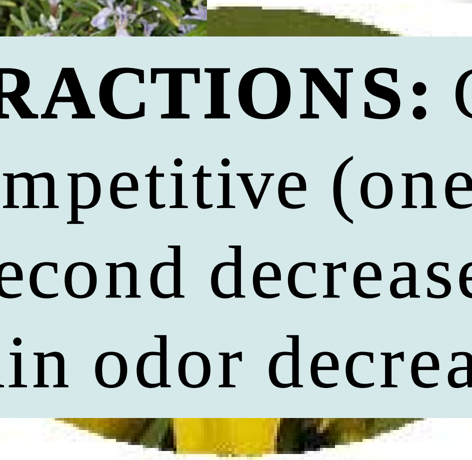
rosmarin

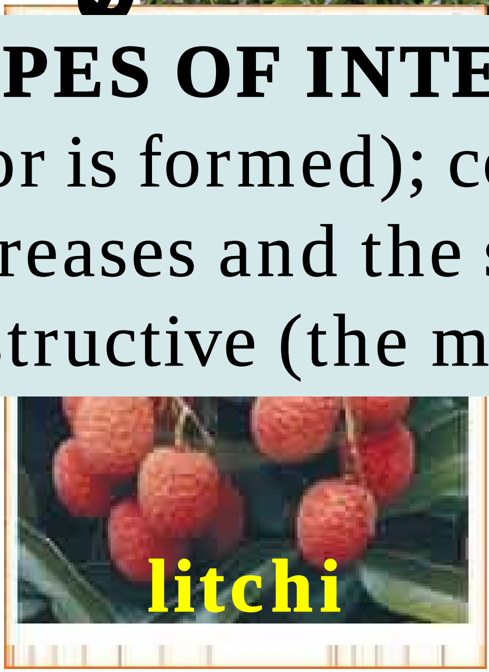
Cre… eraction

+ 3-mercaptohexyl acetate

Passion fruit

Competitive interaction





litchi

TYPES OF INTERACTIONS: Creative (new odor is formed); competitive (one odor increases and the second decreases); destructive (the main odor decreases)

+ acetic acid
+ agressive buffers

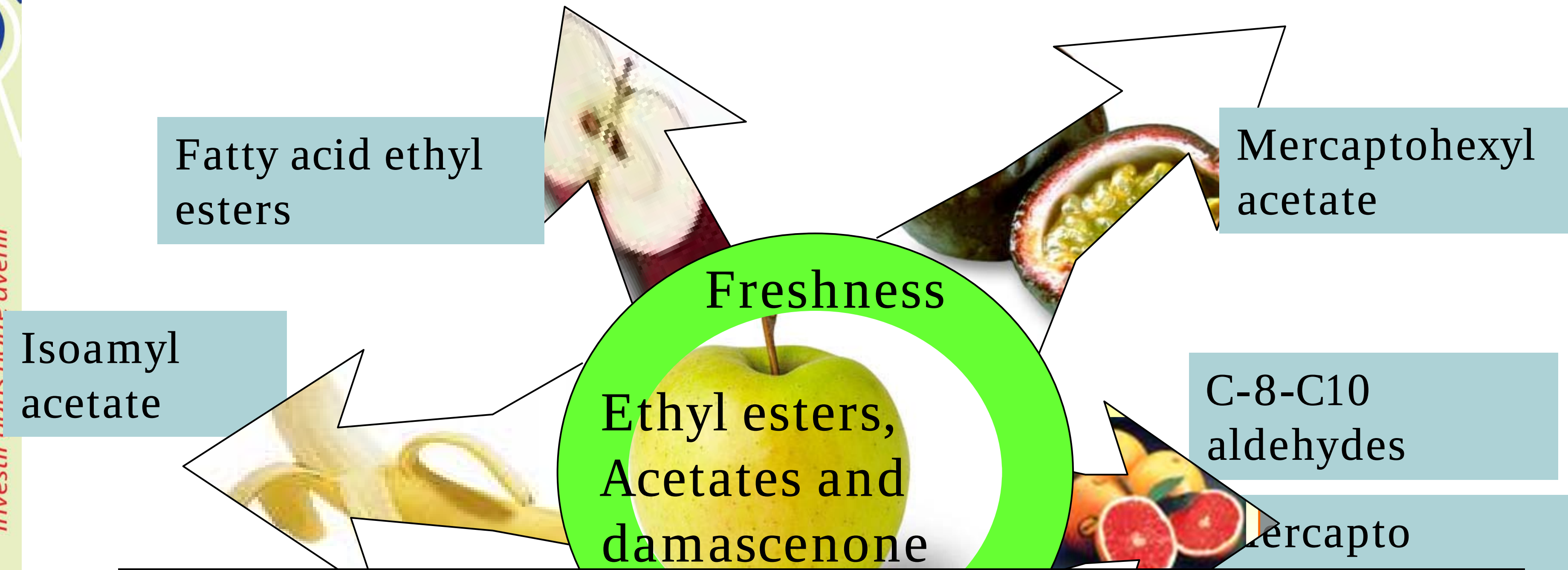
Destructive interaction

Fruity notes in white wines

CREATIVE AND COMPETITIVE INTERACTIONS, whenever the Rule of complexity is fulfilled, the resulting odors will be more interesting

Small amounts of cysteinlyl related aromas and of fermentation volatile acids

Fruity notes in white wines



Fruit note depreciators:

Metoxipirazines
Aldehides
Vinylphenols
Too agressive buffers

Fruity notes in red wines

Mercaptohexyl acetate

peach

-lactones

banana

Isoamyl acetate

Burnt sugar family

Red fruit&caramel

Berry fruit

Enhancement by DMS

Take home messages

- We can claim today that nearly all the most important odorants of wine are well known
- All in all, 47 compounds (16 potential impact compounds plus 10 different families) can be regarded as positive potential contributors to wine aroma nuances, while more than 30 can negatively affect wine quality
- Wine aroma perception depends on the strength of the wine aroma buffer and the wine content on the compounds contributing to the 26 main aroma nuances
- While simple wines can be characterized by having one or two impact compounds, in complex wines aroma nuances are the result of the complex interaction of many chemicals playing roles of impact, major, neat or minor contributors

Take home messages

- Bad aroma compounds are those that induce the suppression of a positive aroma nuance, which can take place at concentration below the recognition threshold
- There are at least 3 aroma enhancers
- Complexity is generally preferred by consumers, and can be found when:
  - A major aroma nuance is due to many different compounds
  - Major wine aroma nuances are due to creative interactions between two or more different aroma vectors
  - Wine aroma nuances are the result of competitive interactions between different aroma vectors

Thanks to all these guys!

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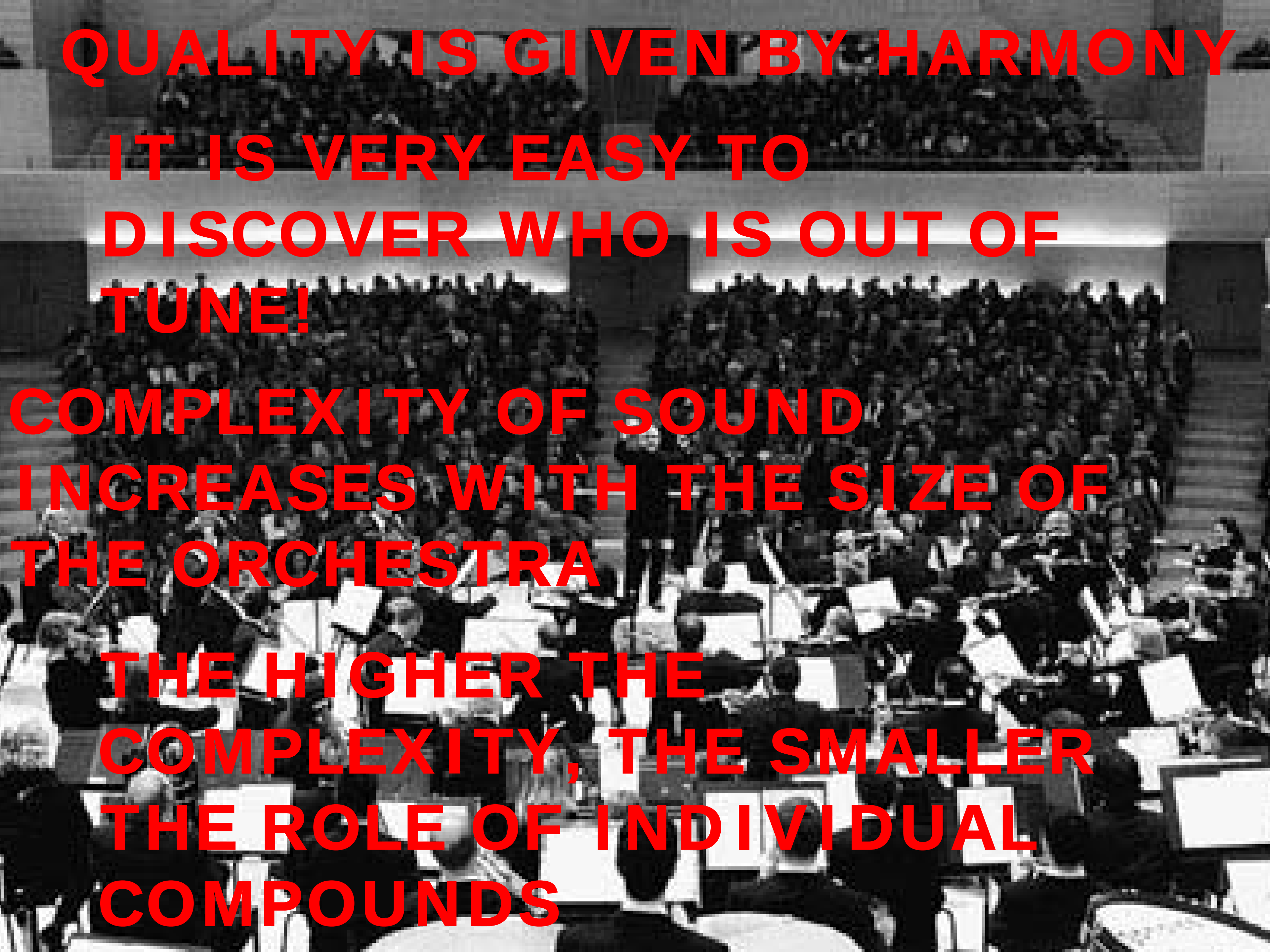
And, please, keep in mind that wine aroma must be understood like...



QUALITY IS GIVEN BY HARMONY

- IT IS VERY EASY TO DISCOVER WHO IS OUT OF TUNE!

COMPLEXITY OF SOUND INCREASES WITH THE SIZE OF THE ORCHESTRA

- THE HIGHER THE COMPLEXITY, THE SMALLER THE ROLE OF INDIVIDUAL COMPOUNDS