The chemical clues of red wine aroma and flavor. Recent developments

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A large scale study about the relationship between red wine composition and its sensory properties has been recently carried out in our laboratories. Some of the most relevant observations and conclusions are presented here and are discussed in reference to our present knowledge about the formation of sensory concepts from chemical inputs. The study has involved the detailed sensory description of three sets of Spanish red wines belonging to three different price segments (Premium; Standard-high; Standard-low), the measurement of quality by a large panel of experts, the chemical analysis of more than 100 aroma compounds and of their polyphenolic composition and the elaboration of synthetic wine models to corroborate the observations.

Quality was in all cases related to the attributes flavor intensity and persistence (by mouth), but only in the Premium class of wines was clearly related to astringency. The relationship between flavor intensity and persistence with astringency, and hence with polyphenolic composition, loosens in the cheaper wine sets, which may suggest that aroma compounds play a role in those attributes in these sets.

Aromatically, the diversity of sensory descriptors increases as well in the lower price-sets. In the Premium class set all the positive descriptors were shared by most samples and significant differences were only found in three negative descriptors. On the contrary, strong divergences in aroma properties were found in the cheaper sets, with 10 and 12 descriptors showing significant differences.

Chemically, quality can be satisfactorily and consistently explained by relatively simple aroma models, being these more complex again in the lower price sets. In all cases quality is positively related to the presence in wine of fruity compounds, some wood extractables, fruity enhancers and negatively to the presence of some volatile phenols, acids and aldehydes.

Some aroma nuances have been also satisfactorily modeled, particularly the fruity notes of the premium wines. The models have revealed the existence of strong perceptual interactions between the odor notes of the different chemical families and some aroma profiles responsible for some odor concepts have been identified. It has been demonstrated that some acid

characteristic is required to have a clear fresh-fruit perception, which explains in simple terms the smaller effect elicited by 4-ethylphenol in some wines. The raisin odor concept has been demonstrated to be caused by fruity esters, β-damascenone and methional, which explains the loose relationship between β-damascenone and the fresh fruit character. Some conclusions about how the aroma complexity of wine should be addressed are drawn.

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UNIVERSITY OF ZARAGOZA

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The chemical clues of red wine aroma and flavor: Recent developments

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Scope and aims

1. To show the latest findings on our interpretation of wine quality and wine sensory properties from the wine content in **odor and flavor-active** compounds
2. Results are derived from a large scale experiment (not yet finished) and are interpreted from our experience and from recent psychophysical research

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The experiment

Spanish Red Wine Price Segments

High (15-25 €) N=25	Average (7-15 €) N=35	Low (<7 €) N=35

MEASUREMENT OF QUALITY BY A PANEL OF EXPERTS (winemakers, wine retailers, sommeliers, wine scientists n>20)

SENSORY DESCRIPTION BY A TRAINED PANEL (n>30; citation frequency from a preselected list of descriptors + quantitative in mouth attributes)

Quantitative analysis of relevant polyphenols (phenolic acids, flavonols, hydroxycinamic derivatives, flavonols, different indexes…)

Quantitative analysis of **ALL** relevant aroma compounds (>105 compounds with 8 different analytical methods)

Complete GC-O profiling	GC-O profiling of just "special" specimens

Quality by segments

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Experts new about the price of the segment
They were asked to freely classify samples in up to five quality groups (1 to 5) attending to **all** the attributes of the samples
Agreement between experts was relatively high

Quality by segments

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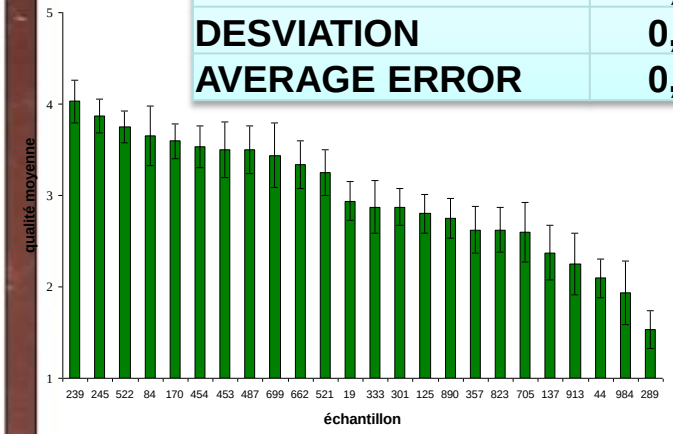
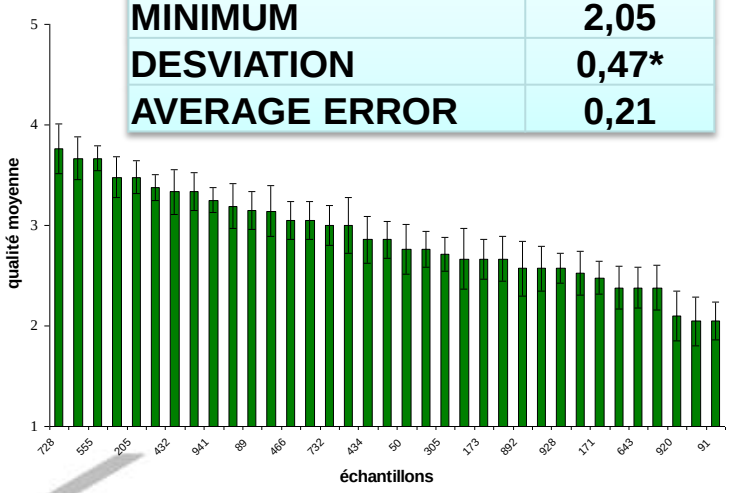
MAXIMUM	4,03*
MINIMUM	1,53
DESVIATION	0,64
AVERAGE ERROR	0,22



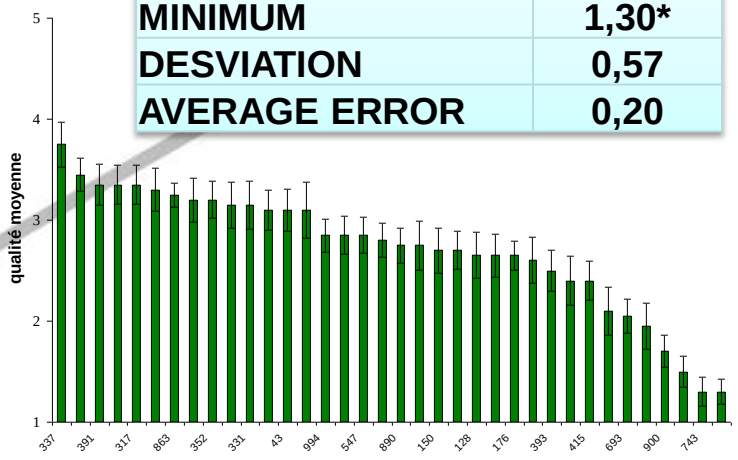
high

MAXIMUM	3,76
MINIMUM	2,05
DESVIATION	0,47*
AVERAGE ERROR	0,21



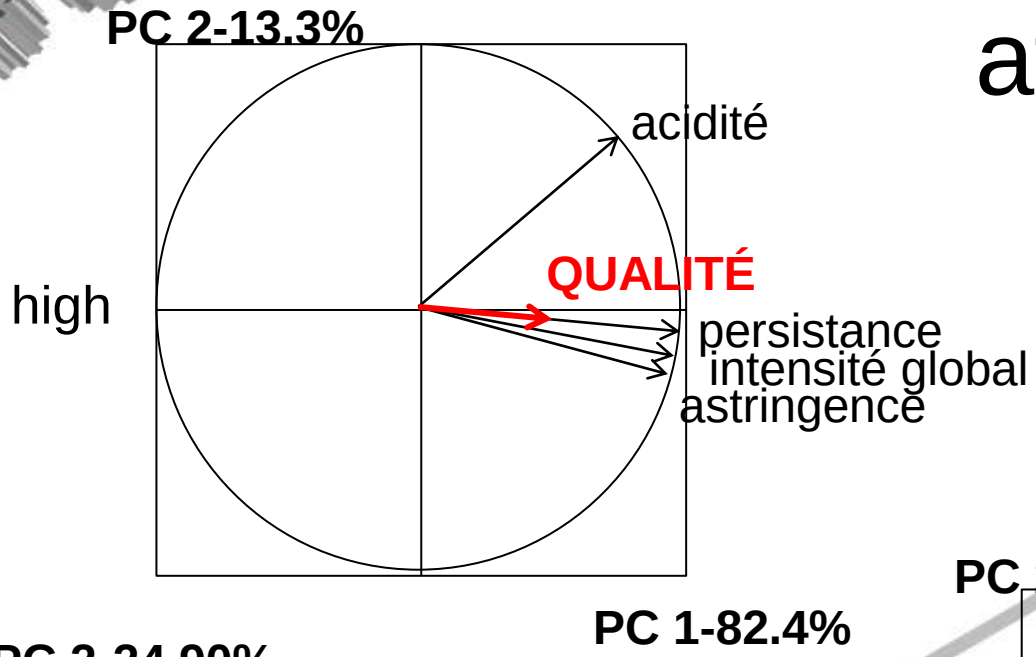
medium

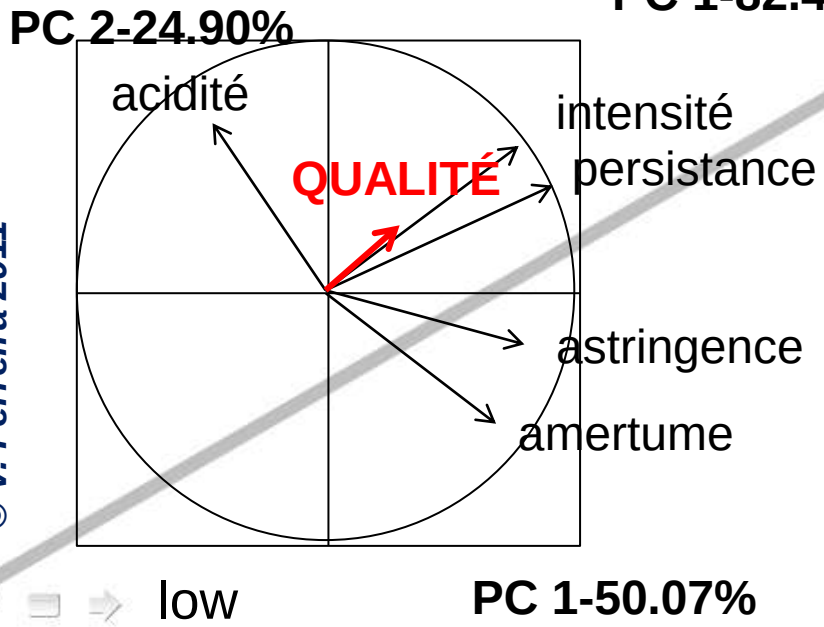
MAXIMUM	3,75
MINIMUM	1,30*
DESVIATION	0,57
AVERAGE ERROR	0,20

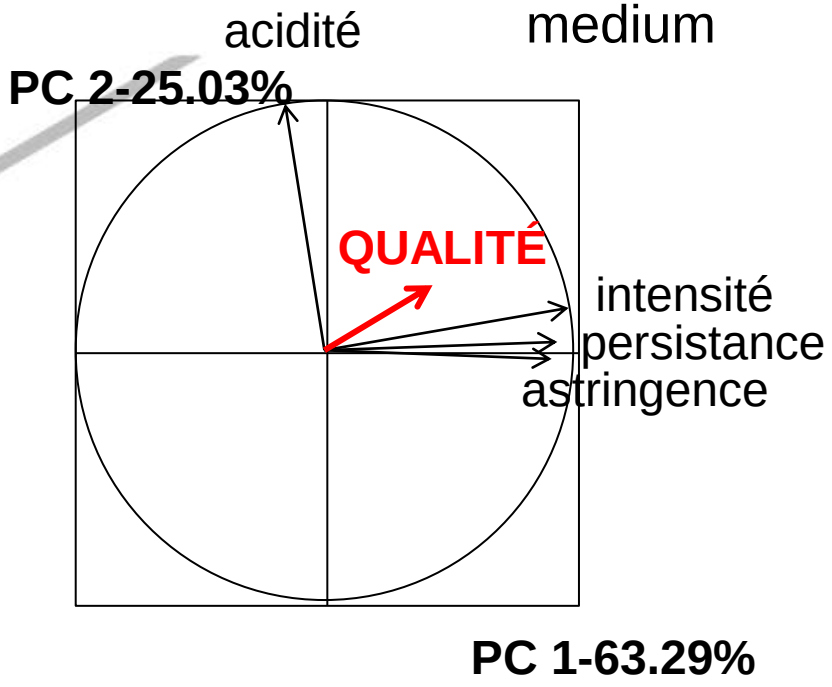


low

Quality and in mouth attributes







Quality and in mouth attributes

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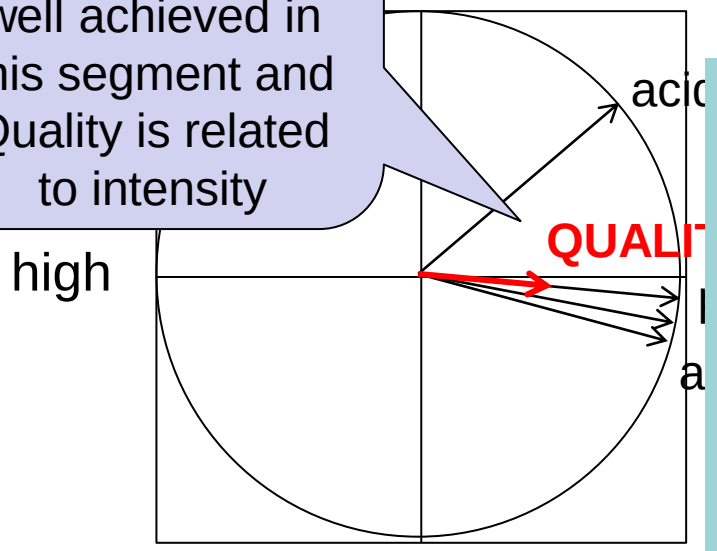
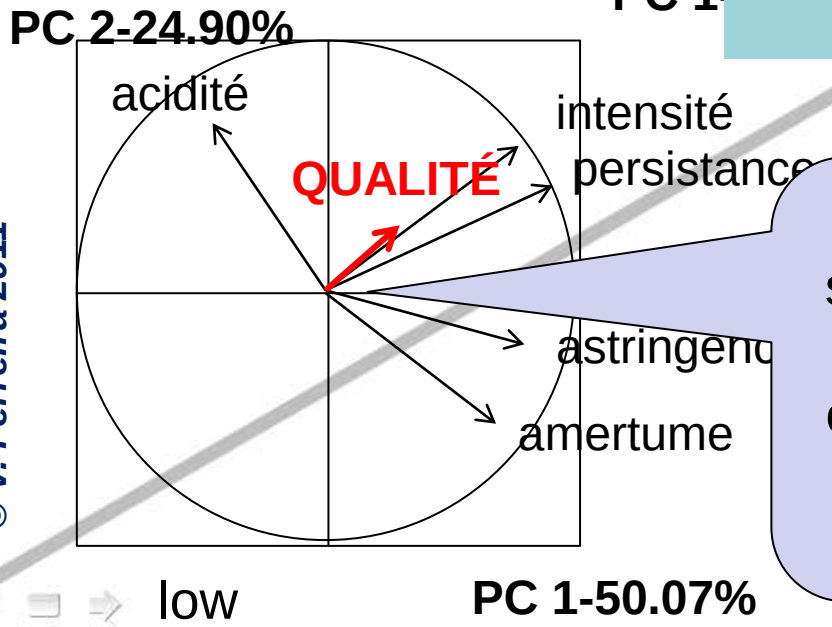
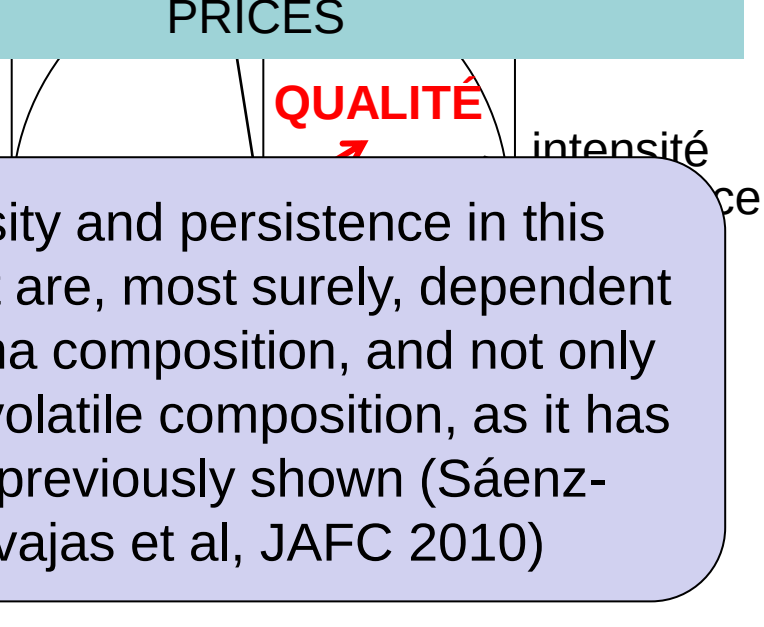
Suggests that flavor balance is well achieved in this segment and Quality is related to intensity

1. QUALITY IS IN ALL CASES STRONGLY RELATED TO GLOBAL INTENSITY AND PERSISTENCE
2. ONLY IN HIGH PRICE WINES, ACIDITY IS RELATED TO QUALITY
3. ONLY IN LOW PRICE WINES, BITTERNESS WAS SIGNIFICANT
4. THE CORRELATION OF ASTRINGENCY WITH QUALITY LOOSENS AT LOWER PRICES

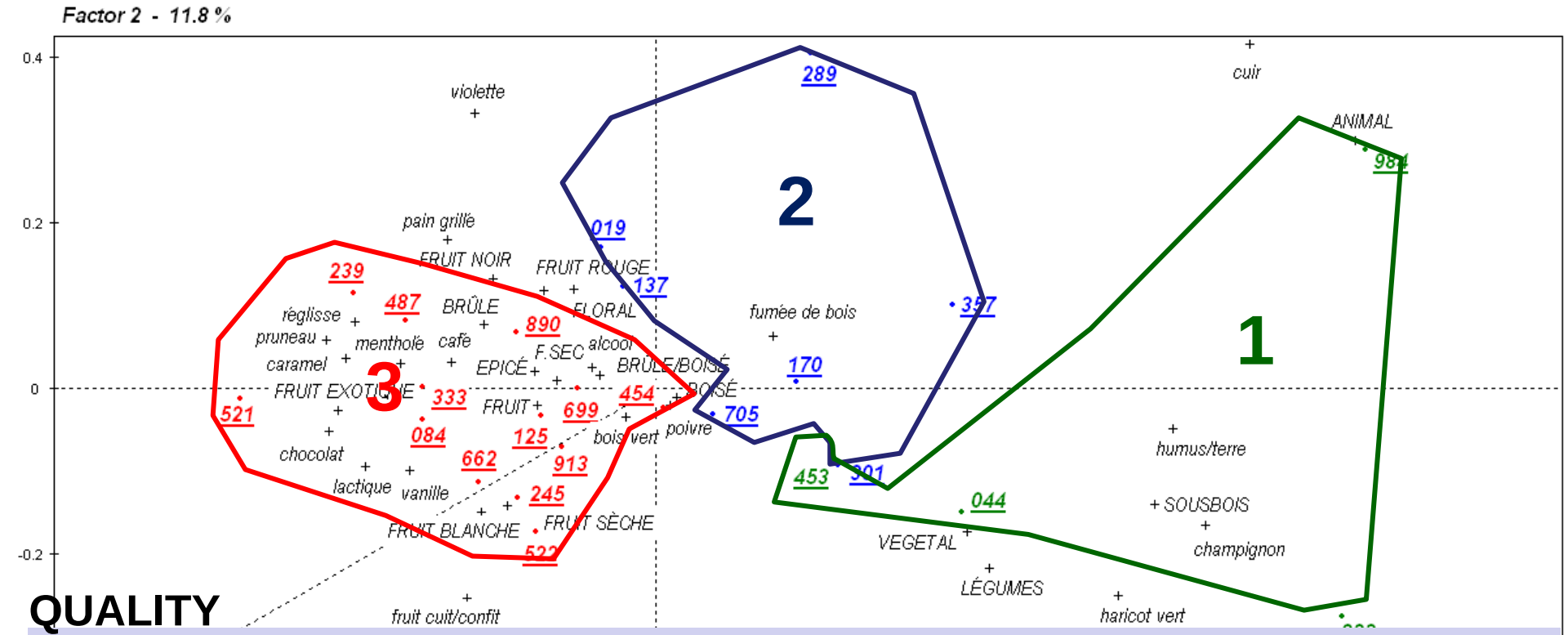






Intensity and persistence in this segment are, most surely, dependent on aroma composition, and not only on non-volatile composition, as it has been previously shown (Sáenz-Navajas et al, JAFC 2010)

Aroma description-high price

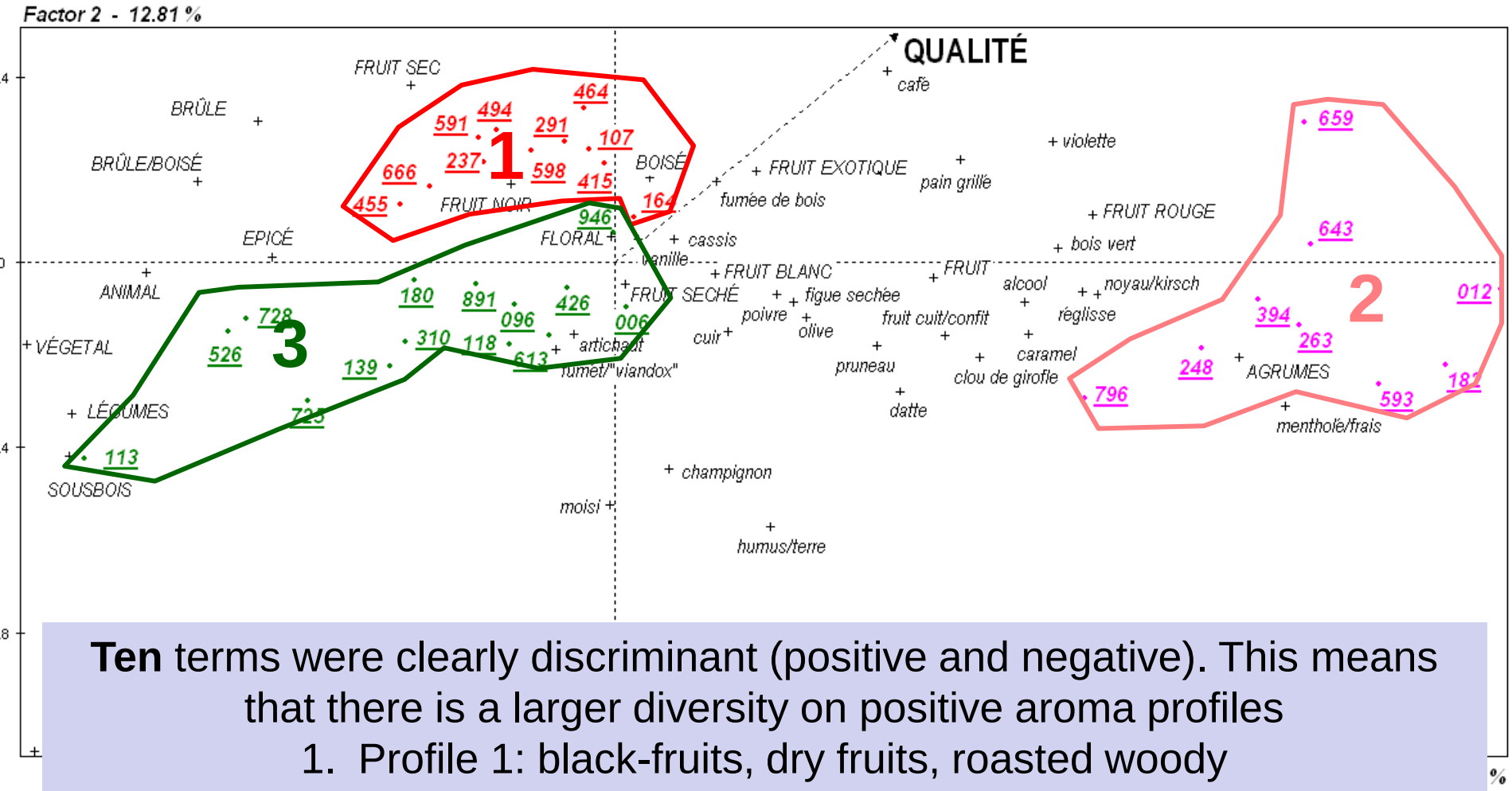


QUALITY

Only three terms were clearly discriminant: animal, leather and bell pepper (this means that quality is essentially related to a major profile with differences of just quantitative nature). In fact, wines form three clusters:

1. deceptive (animal, undergrowth and bell pepper notes);
2. low quality (as before but in competition with fruits)
3. high quality (exotic fruit, candied/cooked fruits, menthol…)

Aroma description-medium price



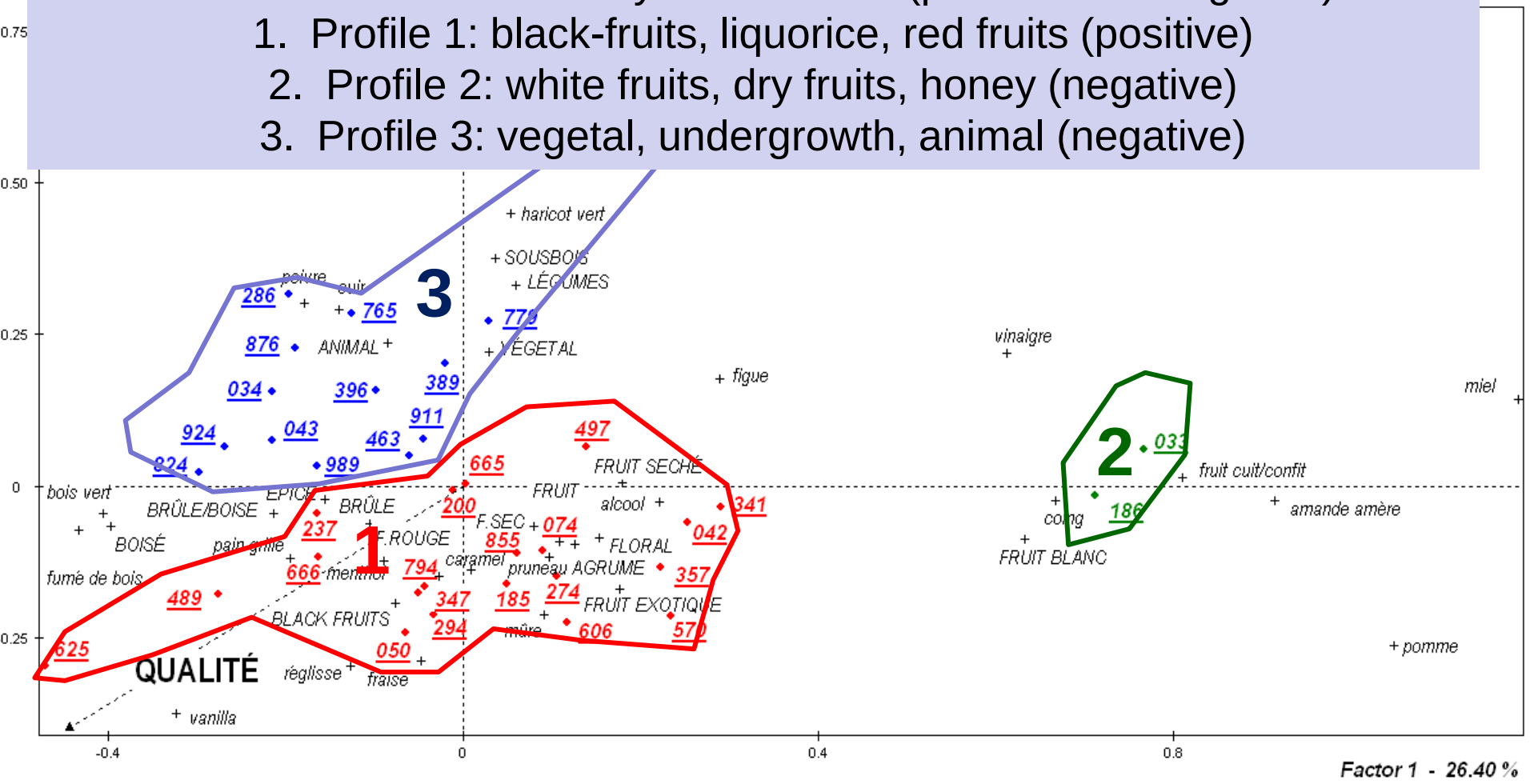
Ten terms were clearly discriminant (positive and negative). This means that there is a larger diversity on positive aroma profiles

1. Profile 1: black-fruits, dry fruits, roasted woody
2. Profile 2: citrus, menthol, red fruits
3. Profile 3 (negative): vegetal, undergrowth, animal

Aroma description-low price

Twelve terms were clearly discriminant (positive and negative).

1. Profile 1: black-fruits, liquorice, red fruits (positive)
2. Profile 2: white fruits, dry fruits, honey (negative)
3. Profile 3: vegetal, undergrowth, animal (negative)



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Modeling quality from aroma chemical composition

Quality in the high price segment:

A Gas Chromatographic-Olfactometric approach

GC-O profiles and quality

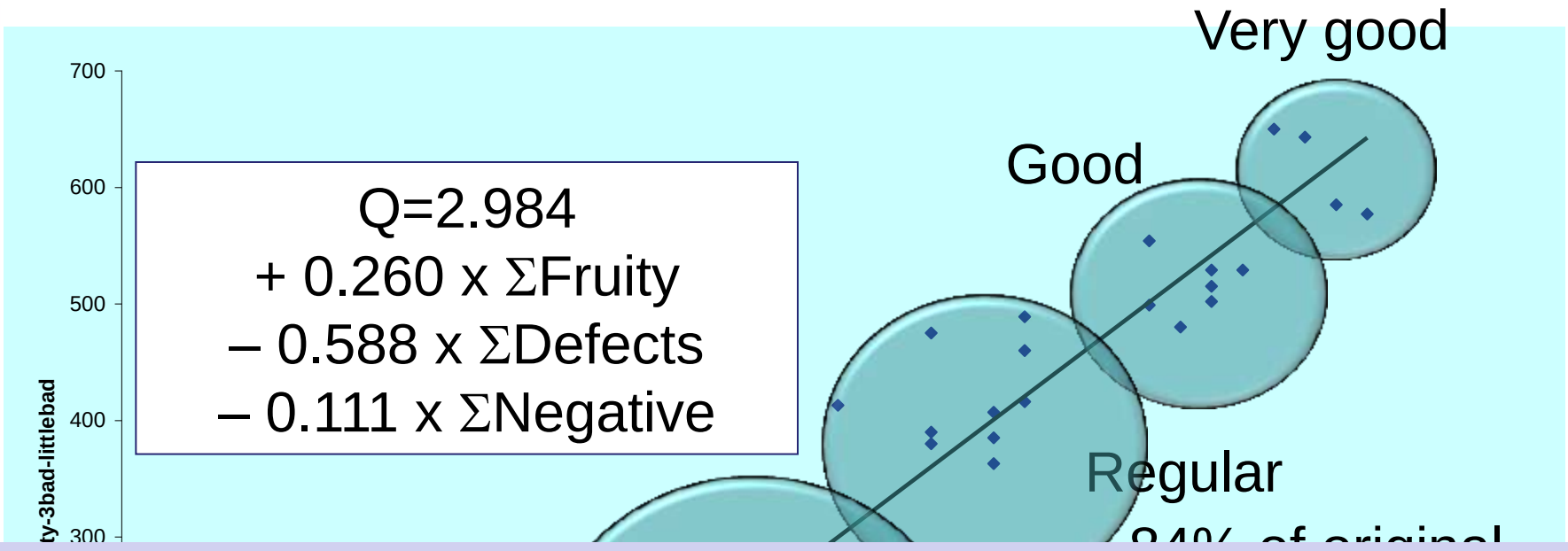
- 65 odorants in the whole
- 33 in all wines
- NO ONE is directly related to Quality
- Some phenols seem to be negatively related to quality
- Odorants classified into the following groups:
  - Fruity (ΣF)
  - Strongly negative –defects- (ΣD)
  - Negative (ΣN)
  - Others (irrelevant in this case)

GC-O profiles and quality

- **Fruity:** 13 esters, β-damascenone and furaneol
- **Strongly negative:** TCA*, 3,5-dimethyl-2-methoxypyrazine*, 4-ethylphenol, 3-ethylphenol, o-cresol
- **Negative:** methionol, methional, Z-2-nonenal, 1-octen-3-one, 2,4-decadienal, 2-methylbutanal, acetic acid, isopropil-2-methoxypyrazine, 2-methylisoborneol*

**These compounds detected in a single sample*

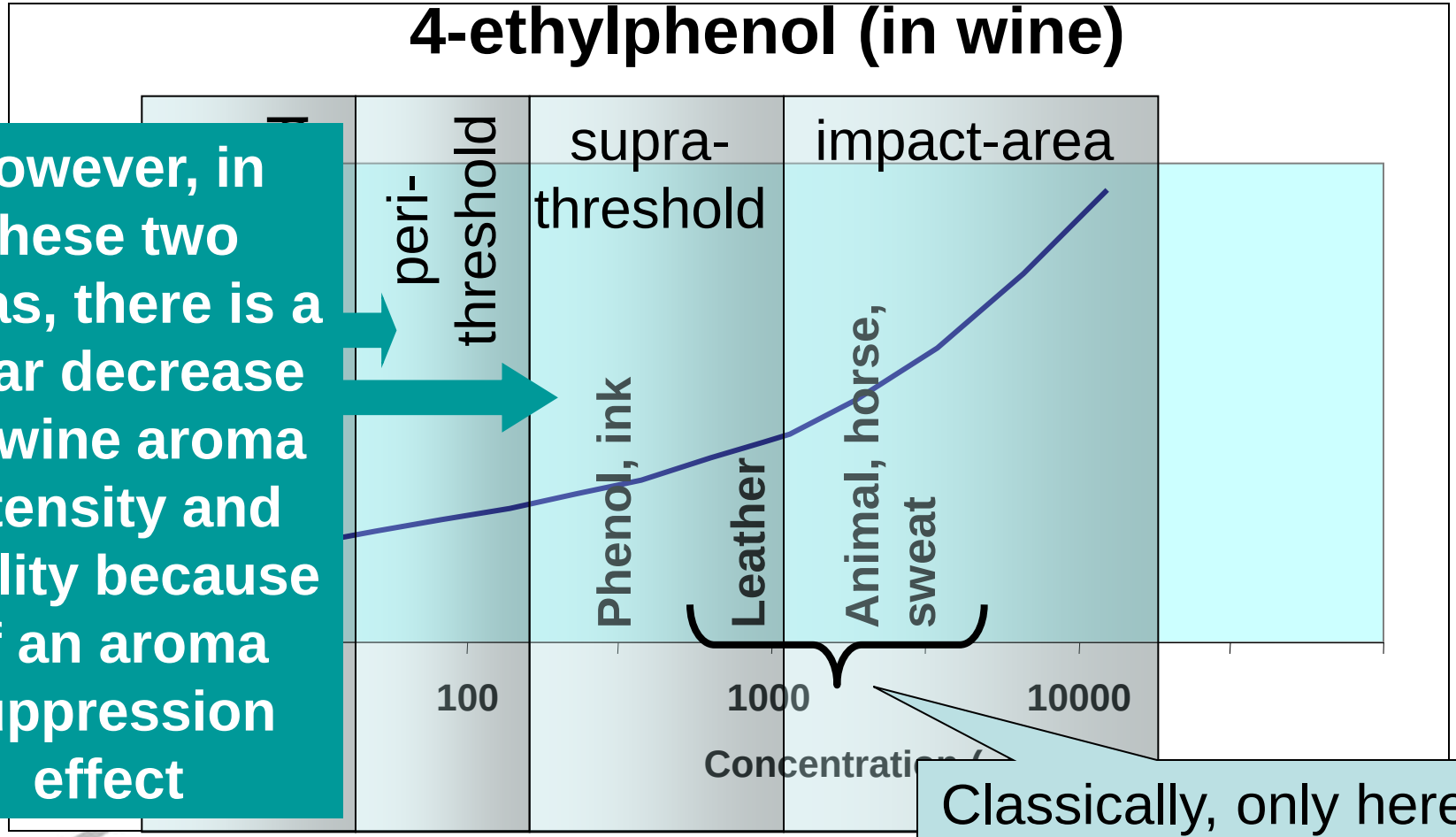
Modeling quality



This extremely simple model seems to enclose a general truth about wine aroma and wine quality:

Although qualitatively/quantitatively fruity aromas are most abundant, the relevance of "fruity depreciators" is critical and these seem to act cooperatively well below their detection thresholds

Perception of off-odors in complex mixtures



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

Classically, only here ethylphenol becomes a problem

Adapted from Aznar et al, JAFC 2003

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Modeling quality from aroma chemical composition

Quality in the high and medium price segments:

Quantitative approach

Experimental details

- Major volatiles analyzed by GC-FID
- “Easy” trace volatiles analyzed by GC-MS
- Volatile Sulfur Compounds analyzed by SPME-GC-pFPD
- gamma-lactones, TCA, minor esters, polar compounds and metoxypyrazines analyzed by GC-MS with **three** specific isolation strategies
- Aldehydes and carbonyls and polyfunctional mercaptans analyzed by **two** different SPE-derivatization and GC-NCI-MS methods
- All in all, 8 different analytical methods and 105 aroma compounds, including **all** those aromatically relevant

Quality and quantitative aroma compos

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Funny thing: these are not at higher levels in these wines

High price (58% explained variance)

Me… expla…

NEGATIVE CONTRIBUTORS

- 4-ethyl phenol
- acetic acid
- phenylacetaldehyd
- methional

NEGATIVE CONTRIBUTORS

- *fusel alcohols ;* 4-ethylphenol
- …ylacetaldehyde; acetic …*acids,* methional, …razines

It should be remarked that these models are absolutely consistent with all the previous ones

POSITIVE CONTR…

- wood extractabl…
- furaneols
- acids
- norisoprenoids
- *ethyl esters*

…ONTRIBUTORS

- …actables
- …enoids
- …hed ethyl esters
- isoamyl acetate , cinnamates, terpenes

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Modeling some aroma notes

Fruity notes in high price red wines

The fruity model

- Explained variance: 73 %

ntributors

- d ethyl
- ters
- ate
- d ethyl esters
- Fura ols
- Linear acids
- Branched acids

??

Negativ

- Met
- Phe
- Acetic
- 4-ethylph
- Norisoprenoids

?

A positive effect of acids, particularly of branched acids, on wine frutiness sounds quite bizarre

A negative effect of nor isoprenoids (β-damascenone and β-ionone) on wine frutiness was completely unexpected

The role of acids on wine fruitiness

Two different red wine models (dearomatized red wine, partially rearomatized with fruity esters (blue) and with fruity esters and b-damascenone (red)) are added with different levels of the acids and ranked attending to fruitiness

Level of addition	0	Min	Median	Maxima	Significance
Linear acids		Fruity base 1 (without damascenone)			
		Fruity base 2 (with damascenone)			
Branched acids		Fruity base 1 (without damascenone)			
		Fruity base 2 (with damascenone)			
Both		Fruity base 1 (without damascenone)			
		Fruity base 2 (with damascenone)			
Acetic		Fruity base 1 (without damascenone)			
		Fruity base 2 (with damascenone)			

How can these results be interpreted?

- Fruitiness is what we call an “odor concept” derived from our experiences with natural fruits
- Most real fruits have some volatile acids in their aroma composition and have also “fresh” character
- It makes sense that having some acids makes the smell to become closer to that of our personal odor concept
- β-damascenone plays an outstanding pivotal role, making the perceptual interaction stronger
- Acetic acid, on the contrary is linked in our memories to rotten fruit, making the fruity perception to decrease

The complex role of β-damascenone

Why β-damascenone in the model had a negative coefficient?

Level of addition	0	Min	Median	Maxima	Significance
β-damascenone	Fruity base 1 (without damascenone)				

Because there is an optimum value!! From a certain point increasing amounts do not bring about any increment in fruitiness !!!

What happens then with wine aroma with those increasing amounts?

The complex role of β-damascenone

These effects were far less intense in the absence of β-damascenone!!!
These means that β-damascenone contributes to:

1. **The fresh fruit character**
2. **The raisin character**
3. **The honey character**

ficient?

Additions to a model containing β-damascenone					ficance
Raisin note + methional	10	-	23	22	>99%
HONEY note + phenylacetaldehyde	11	15	23	33	>99%

The answer is many things: β-damascenone increases raisin notes and oxidized (honey) character, by itself and by interaction with methional and phenylacetaldehyde

How can these results be interpreted?

- These results should be interpreted in terms of odor concepts and odor objects
- Odor concepts are intrinsically linked to specific odor profiles, as Thomas-Danguin and collaborators have recently shown (Le Berre et al, 2008 and 2010) and as perfumers have always known
- At least three relevant odor concepts of wine (fresh fruit, raisin, honey-cooked fruit) are contributed by the same odor components in different proportions, being β-damascenone one of the major pivotal points
- Altering the proportions of β-damascenone may result on moving from one odor object (fresh fruit) to other (raisin)

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Modeling some aroma notes

Animal notes vs. fruity notes in high price red wines

The animal model

- Explained variance: 60 %

Positive Contributors	***Negative Contributors***
• 4-ethylphenol • 4-ethylguaiacol	• Ethyl esters • Isoam A i

The positive effect of esters and norisoprenoids was noted in previous models (Aznar et al, JAFC 2003)

The strange "protecting" effect of branched acids has been recently suggested (Romano et al, FC 2009)

Here, we rather wonder whether a stronger fruity character makes higher levels of ethyl phenols tolerable

Checking the interaction animal x fruitiness

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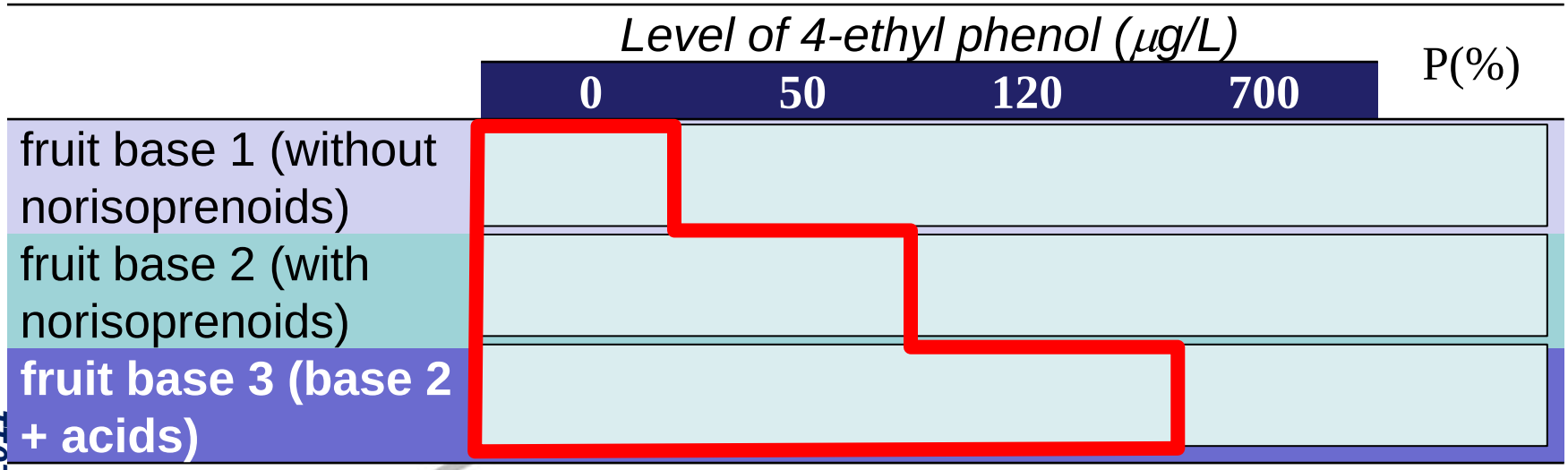
RANKING TEST FOR FRUITY AROMA: Effect of the additions of 4-ethyl phenol on different wine models



It is evident that in the models with higher fruity character, higher levels of ethyl phenol are tolerable!!

Interpreting this result

- This result can be interpreted from classical psychophysical work on simple odor mixtures
- As was previously shown, nor-isoprenoids and acids are part of the fruit concept, which implies that the addition of these compounds increase not only the quality, but also the intensity of its fruitiness
- Higher intensity means that a higher level of 4-ethyl phenol is required for having the animal odor as dominant

Take home messages

- Wine quality is strongly related to the intensity and persistence perceived by mouth in all cases, but its relationship with astringency loosens in the cheaper cases
- The most expensive wines had a consistent aroma profile and relationship with quality was mainly of quantitative nature. In the other segments, most diversity in profiles was observed
- Consistent models for quality have been produced. In all cases quality is related to the wine content in positive aroma compounds and negatively with the content in aromas of negative character, which seems to act cooperatively even below threshold

Take home messages

- The perception of fruitiness in the most expensive Spanish red wines is positively related not only to their content in fruity compounds, but also to their content in volatile acids (excluding acetic).
- Fruitiness is negatively related to some known off-odors, such as ethylphenols or aldehydes. The role played by b-damascenone is quite complex
- This compound, together with fruity compounds and acids, is responsible for fresh fruit notes, but at higher levels or in cooperation with methional or phenylacetaldehyde, produces raisin or honey notes
- Finally, the contribution of acids to fruitiness, can help explaining why wines containing high levels of these compounds can tolerate higher levels of ethylphenols without becoming off-flavored

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