Simposio: 'Maturazione dell'uva e qualità del vino'

Oristano, 31 marzo 2006

La componente aromatica dei vini bianchi: varietà, ambiente, tecnica ed evoluzione

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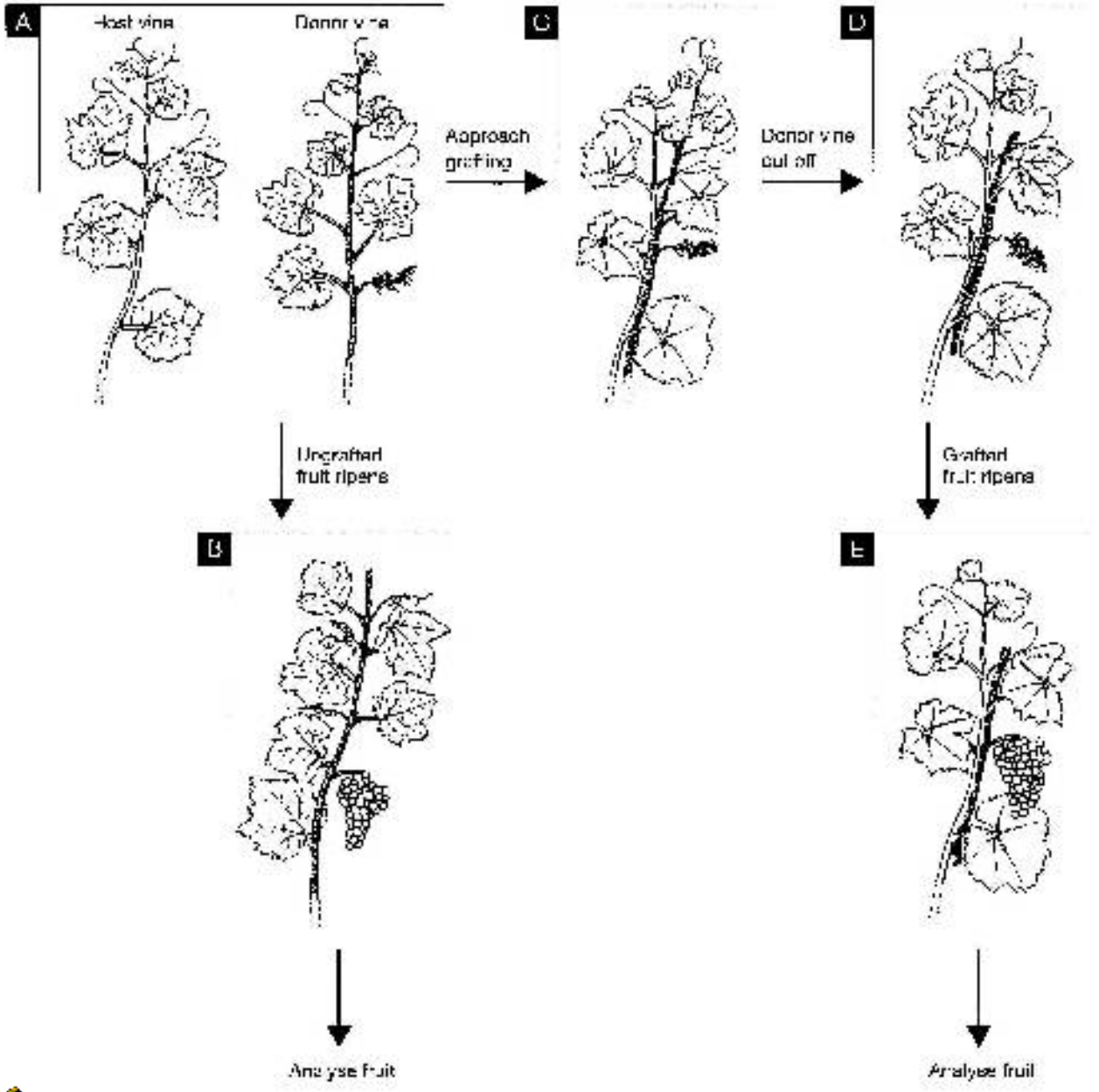
Aroma compounds analysis

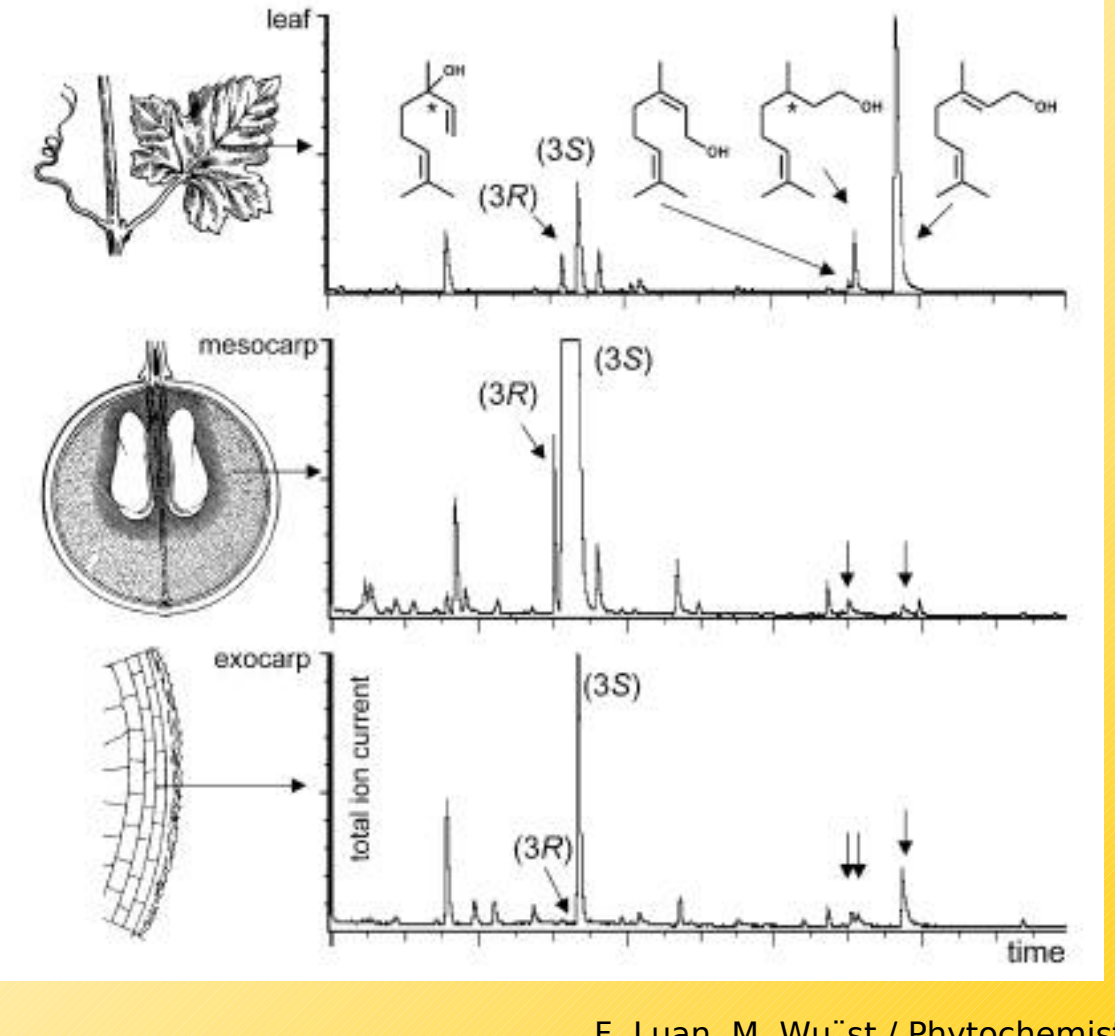
The cases here considered:

- *Muscat-called varieties sub-grouping;*
- *discrimination of wines from White Riesling German crosses;*
- *profile comparison between products of different European regions;*
- *peculiarities of some non-floral varieties of Italy;*
- *influence of the technology (e.g. grape drying phase and duration) to produce special markers: the case of Vino Santo del Trentino and Recioto di Soave*



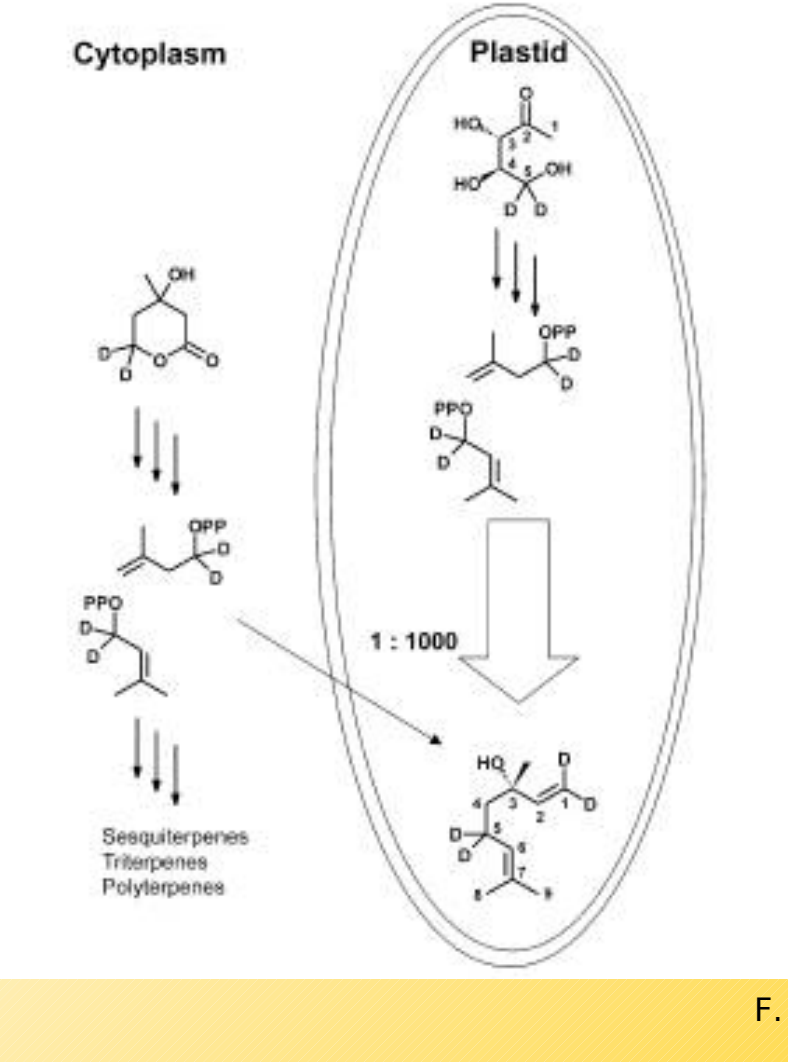
Example of tranfer of grape bunches by approach-grafting to verify the aroma expression "inheritance" at cluster level (Gholami *et al.*, 1995)

Distribution of the main monoterpene alcohols linalool, nerol, citronellol and geraniol in different organs and tissues in Vitis vinifera cv. Muscat Ottonel.



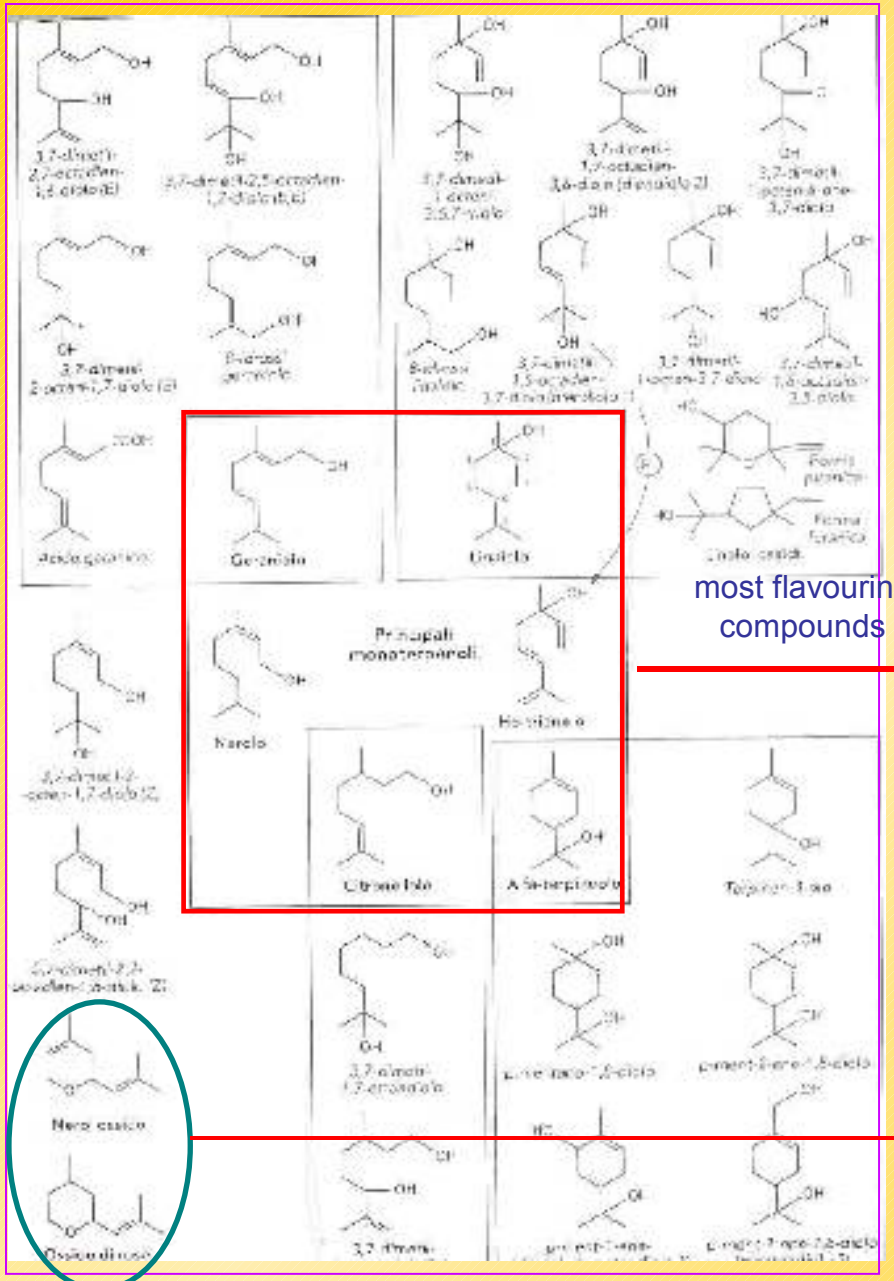
F. Luan, M. Wu¨st / Phytochemistry 60 (2002) 451–45

Expected labelling pattern of (3S)-linalool upon incorporation of two units [5,5-2H2]-DOX and compartmentation model of monoterpene biosynthesis in grape.



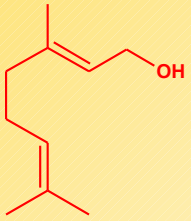
F. Luan, M. Wu¨st / Phytochemistry 60 (2002) 451–45

Main monoterpenols in grapes



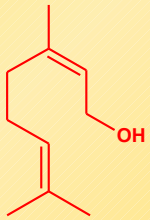
(P. Ribéreau-Gayon et al.:Traité d'oenologie, 1998)

most flavouring compounds



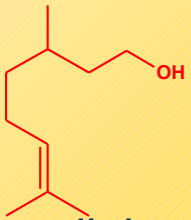
geraniol

linalool

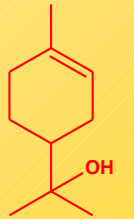


nerol

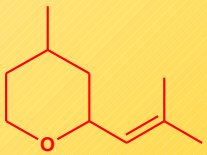
Ho-trienol



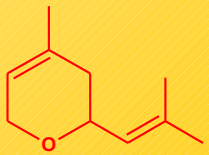
citronellol



α-terpineol



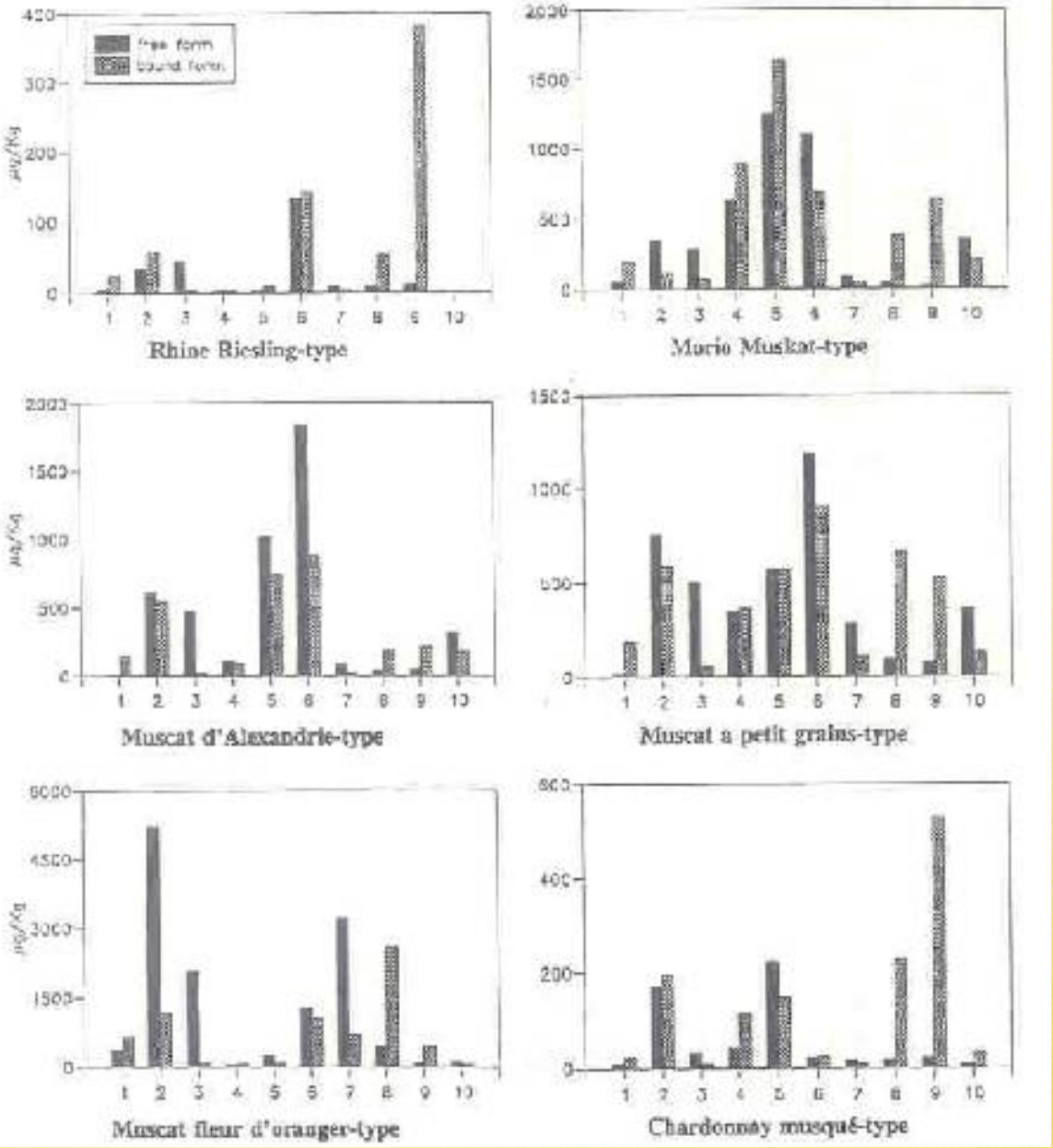
rose oxide



nerol oxide

Free and bound aroma profiling of Muscat-called variety subgroups

(41 varieties, 3 vintages for the same vineyard, PCA groupings, histogramms based on most significant variables from the stepwise analysis applied for LDA)



1. ***tr.*** **F .linal. oxide**
2. **Linalool**
3. ***tr.*** **P.linal. oxide**
4. **Nerol**
5. **Geraniol**
6. **Ho-diol I**
7. **Ho-diol II**
8. ***tr.*** **8-OH-linalool**
9. ***cis*** **8-OH-linalool**
10. **7-OH-geraniol**

G. Versini et al., 1993. Proceed. Intern. Symposium on: "Conaissance aromatique des cépages et qualité des vins" pp. 12-21.

Aroma enrichment technique

II° 15 ml WATER

III° 30 ml CH_2Cl_2

I° 50 ml wine+ 50 ml H_2O

IV° 30 ml CH_3OH

Solid phase extraction with ISOLUTE ENV+® cartridge

(by using XAD-2 phase, different volumes and kind of solvents are used)

ISOLUTE® SPE
ENV+ Cartridge 1g/6 ml

30 ml CH_2Cl_2 → concentration → GC-MS analysis

30 ml CH_3OH → enzymatic reaction → GC-MS analysis

variety	symbol	production region	vintage	notes	n° of samples
Rhine Riesling	R	D/Palatinate	94	3 wineries; 2 quality types	3
Silvaner	Y	D/Palatinate	90-93-94	4 wineries; 2 quality types	5
Scheurebe	S	D/Palatinate	93-94	4 wineries; 2 quality types	6
Mueller-Thurgau	M	D/Palatinate	94	5 wineries; 1 quality types	5
Bacchus	B	D/Palatinate	91-92-93-94	2 wineries; 2 quality types	5
Ehrenfelser	E	D/Palatinate	91-92-93	2 wineries; 2 quality types	3
Kerner	K	D/Palatinate	90-91-94	4 wineries; 3 quality types	5
Rhine Riesling		I/South-Tyrol	95	all different wineries	7
Silvaner		I/South-Tyrol	95	all different wineries	5
Mueller-Thurgau		I/South-Tyrol	94-95	6 wineries	14
Manzoni 6.0.13		I/Trentino, Veneto	92-93-94	2 winery; 5 different areas	7

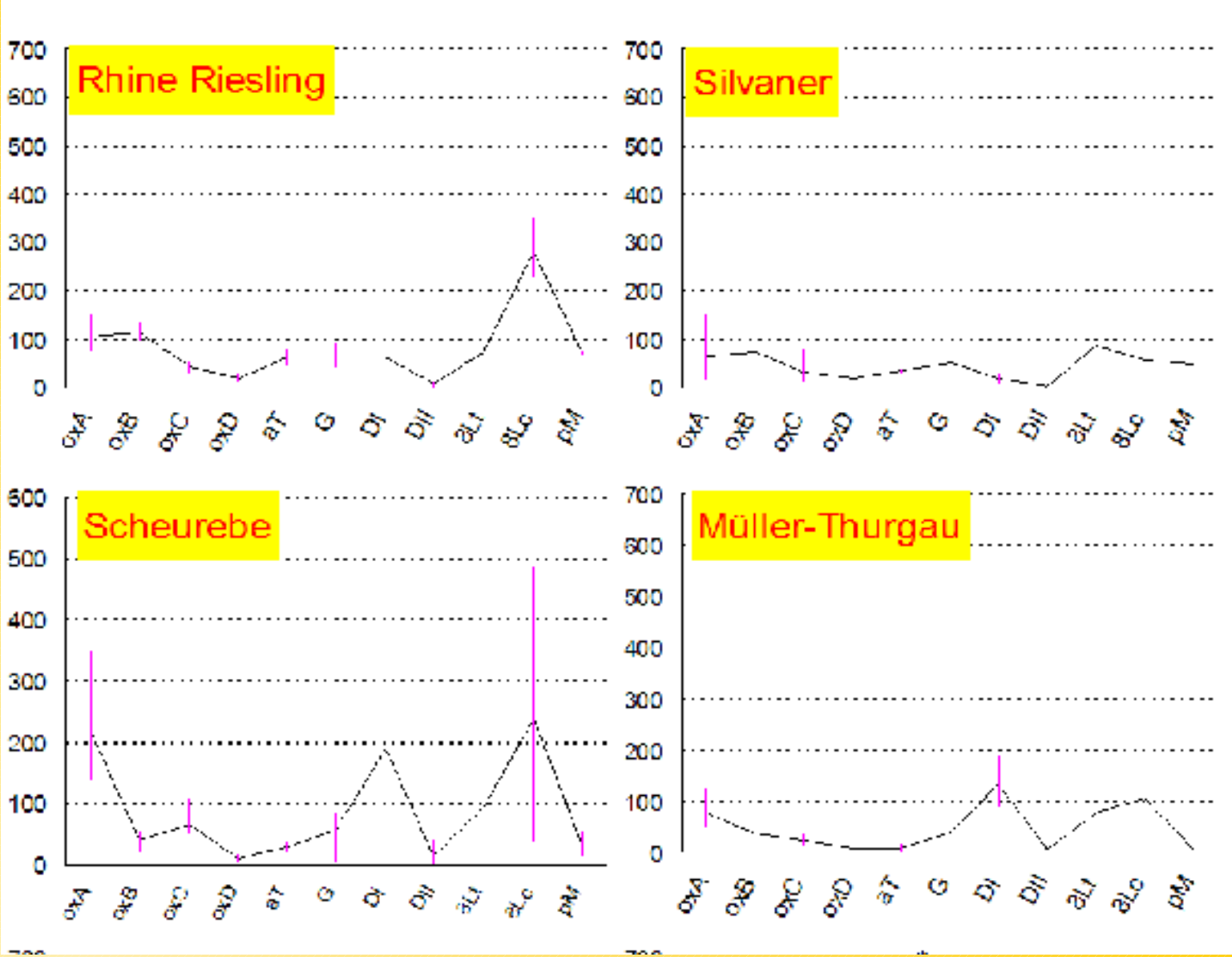
Discrimination of wines from White Riesling German crosses

List and specifications of the analysed monovarietal wines.

G. Versini, A. Rapp, Dalla Serra, G. Nicolini, 1997. In: Proceed. 5th Wartburg Aroma Symp., pp. 269-271

Heterosides monoterpene profile of German varietal wines

(mean, min-max; µg/L)



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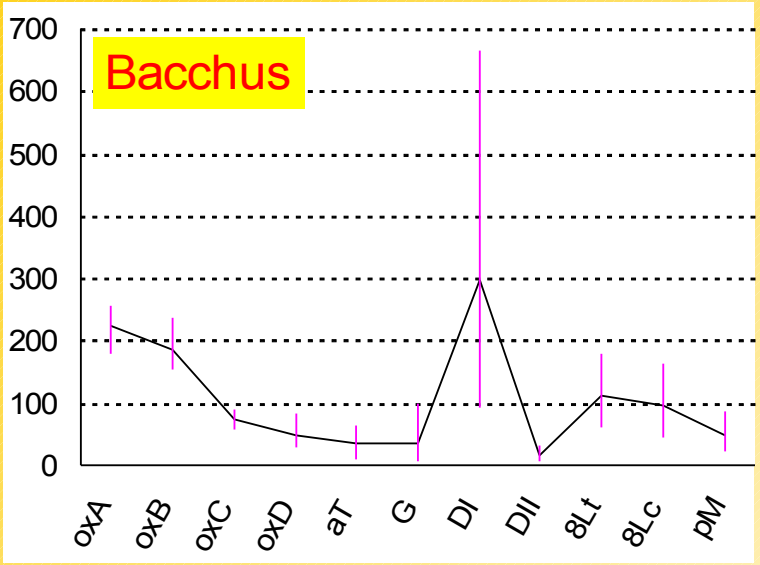
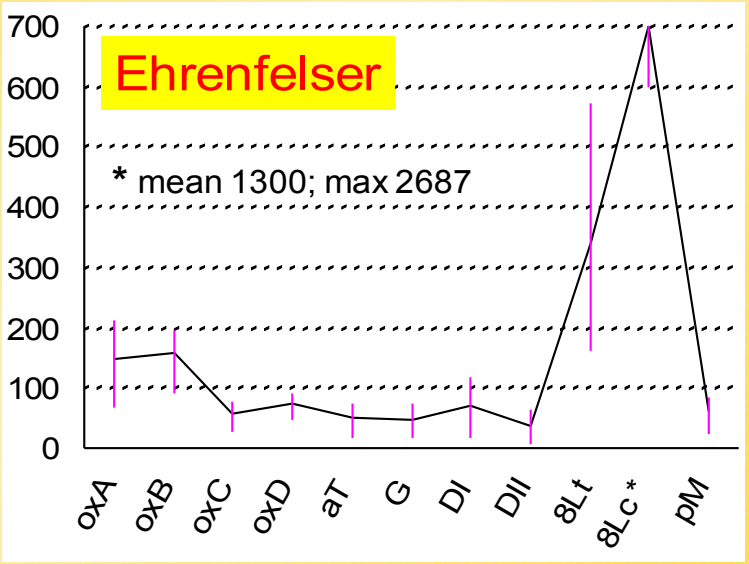
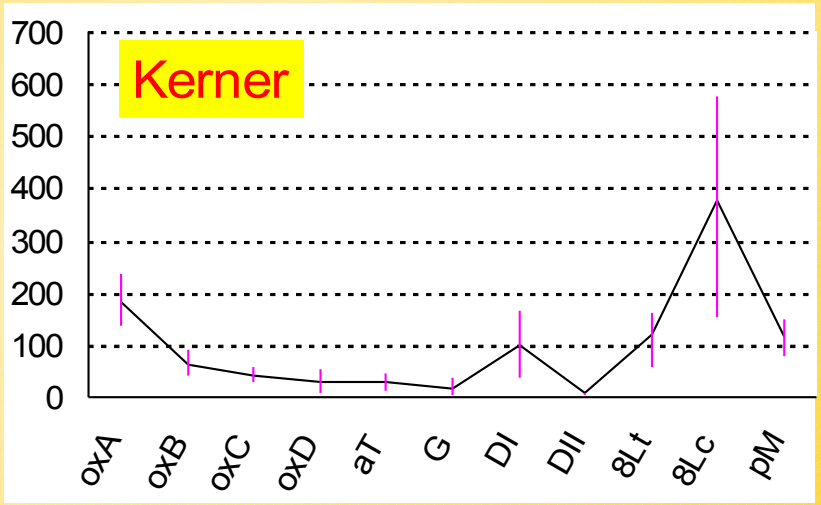
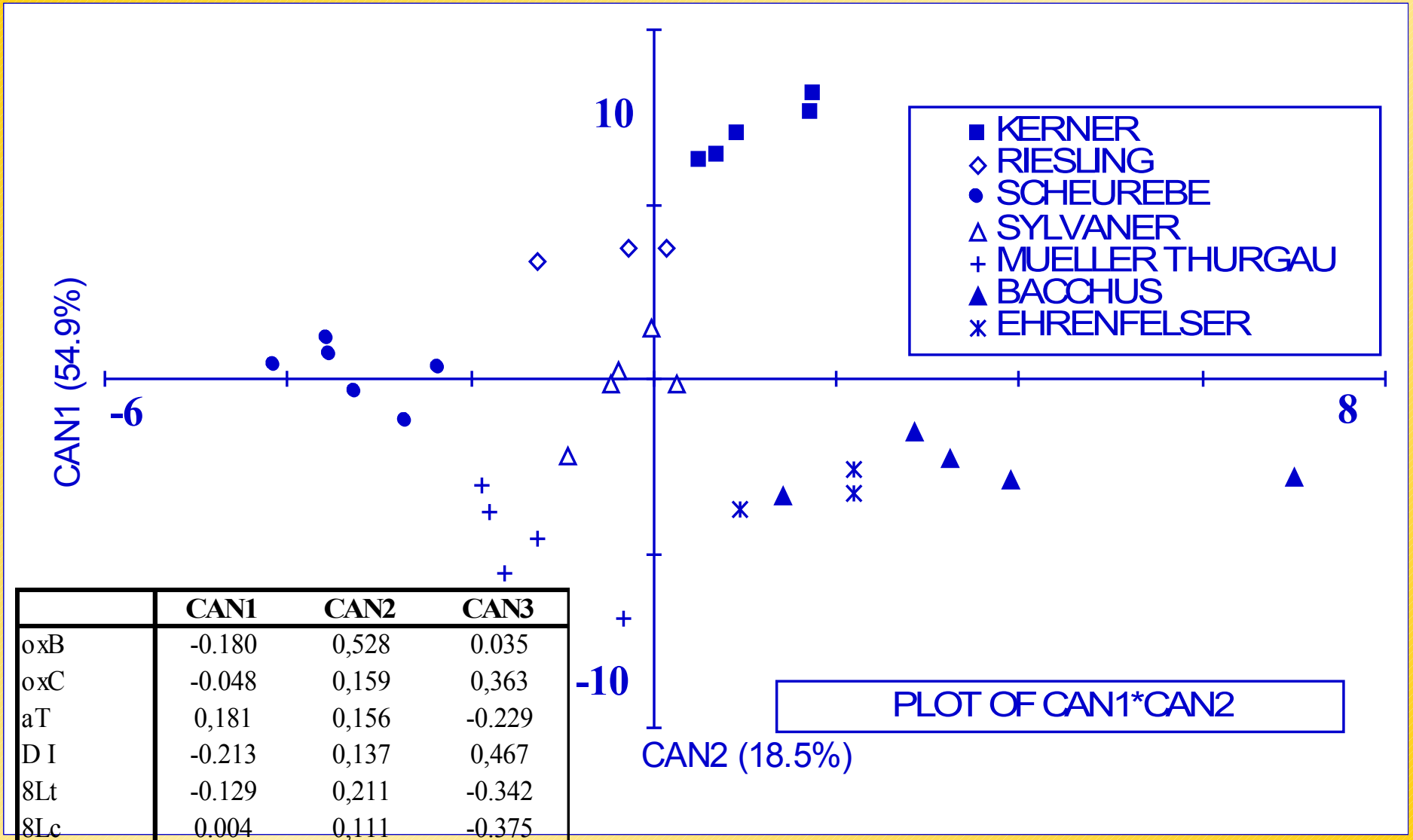




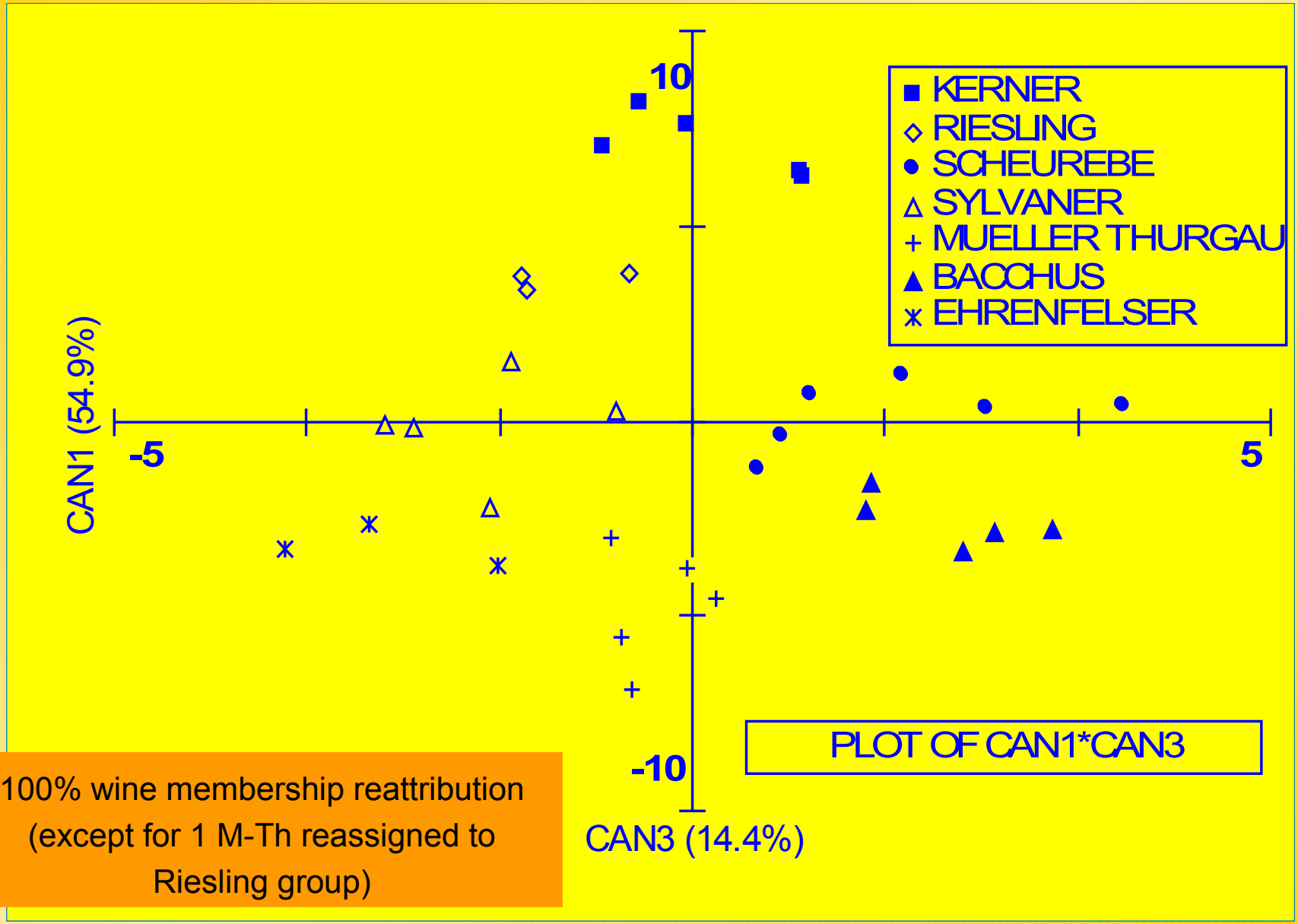


LDA applied to DIFFERENT VARIETAL GERMAN WINES

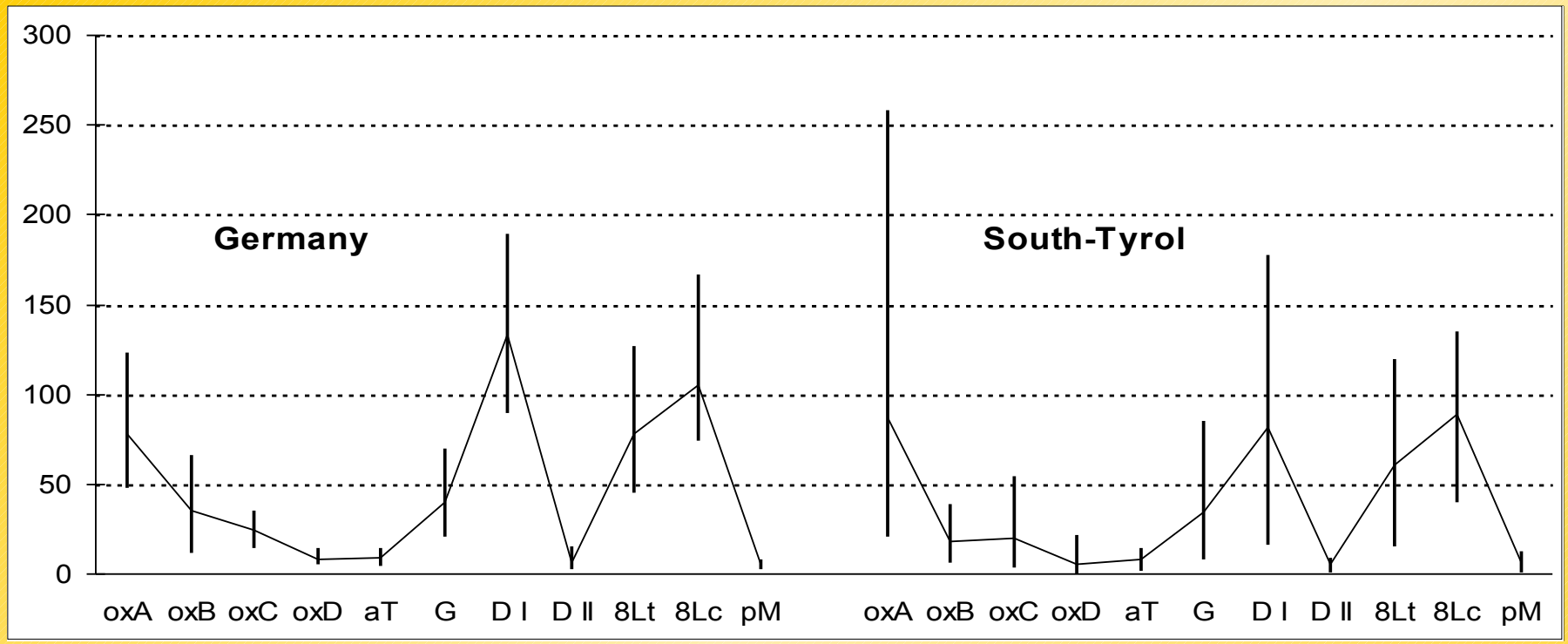


	CAN1	CAN2	CAN3
oxB	-0.180	0,528	0.035
oxC	-0.048	0,159	0,363
aT	0,181	0,156	-0.229
D I	-0.213	0,137	0,467
8Lt	-0.129	0,211	-0.342
8Lc	0.004	0,111	-0.375
7OHG	0,239	0,217	-0.270
nM	0,539	0,283	-0.140

LDA applied to DIFFERENT VARIETAL GERMAN WINES

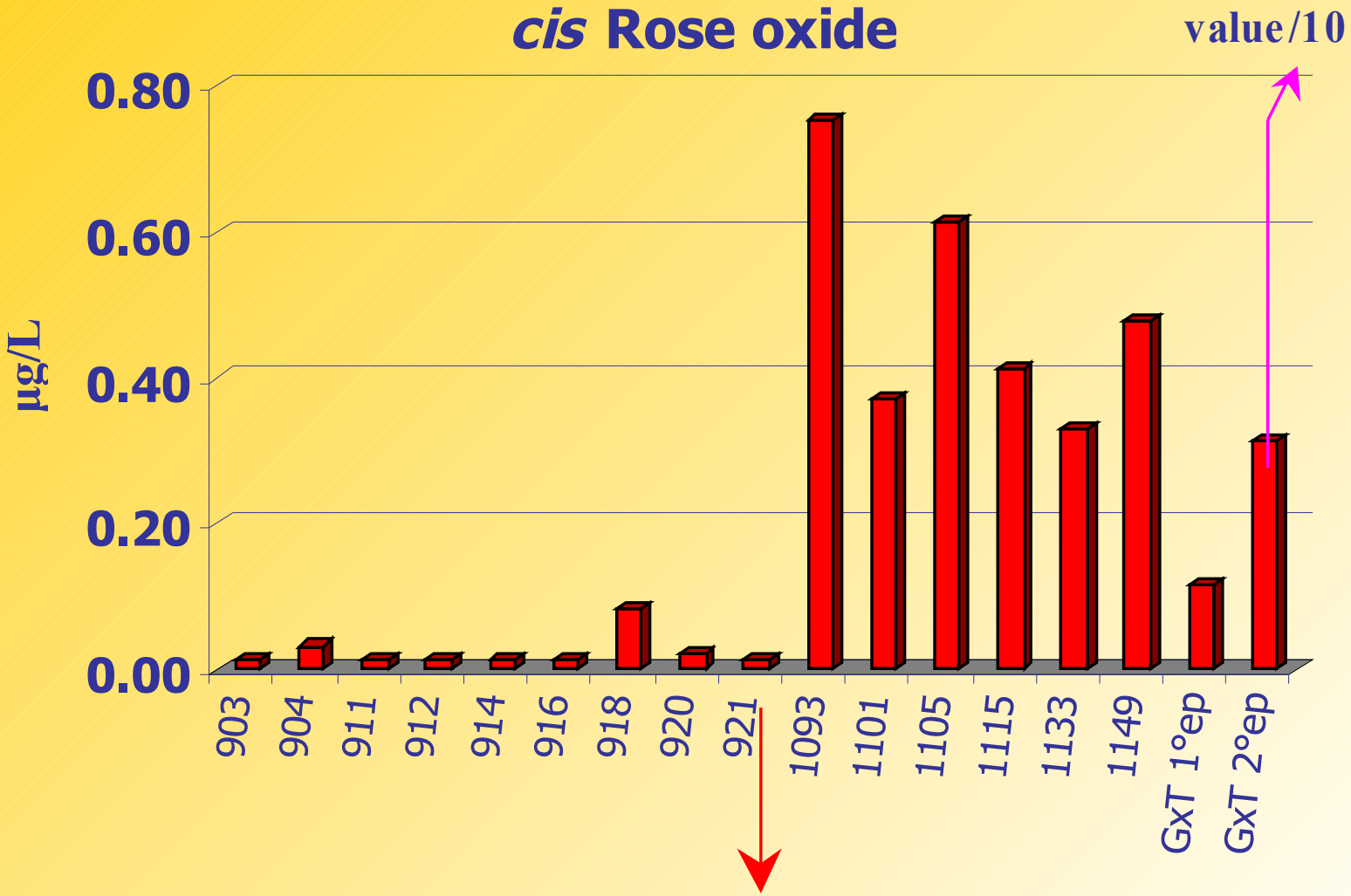


100% wine membership reattribution (except for 1 M-Th reassigned to Riesling group)



Profile comparison of bound aroma compounds (µg/L) in Mueller-Thurgau wines from different grape-growing areas: *evidence of a good similarity*

Variation of some free aroma compounds in 1997 wines from non-official Traminer clones grown in two vineyard at different altitude in the Trentino-South Tyrol region.



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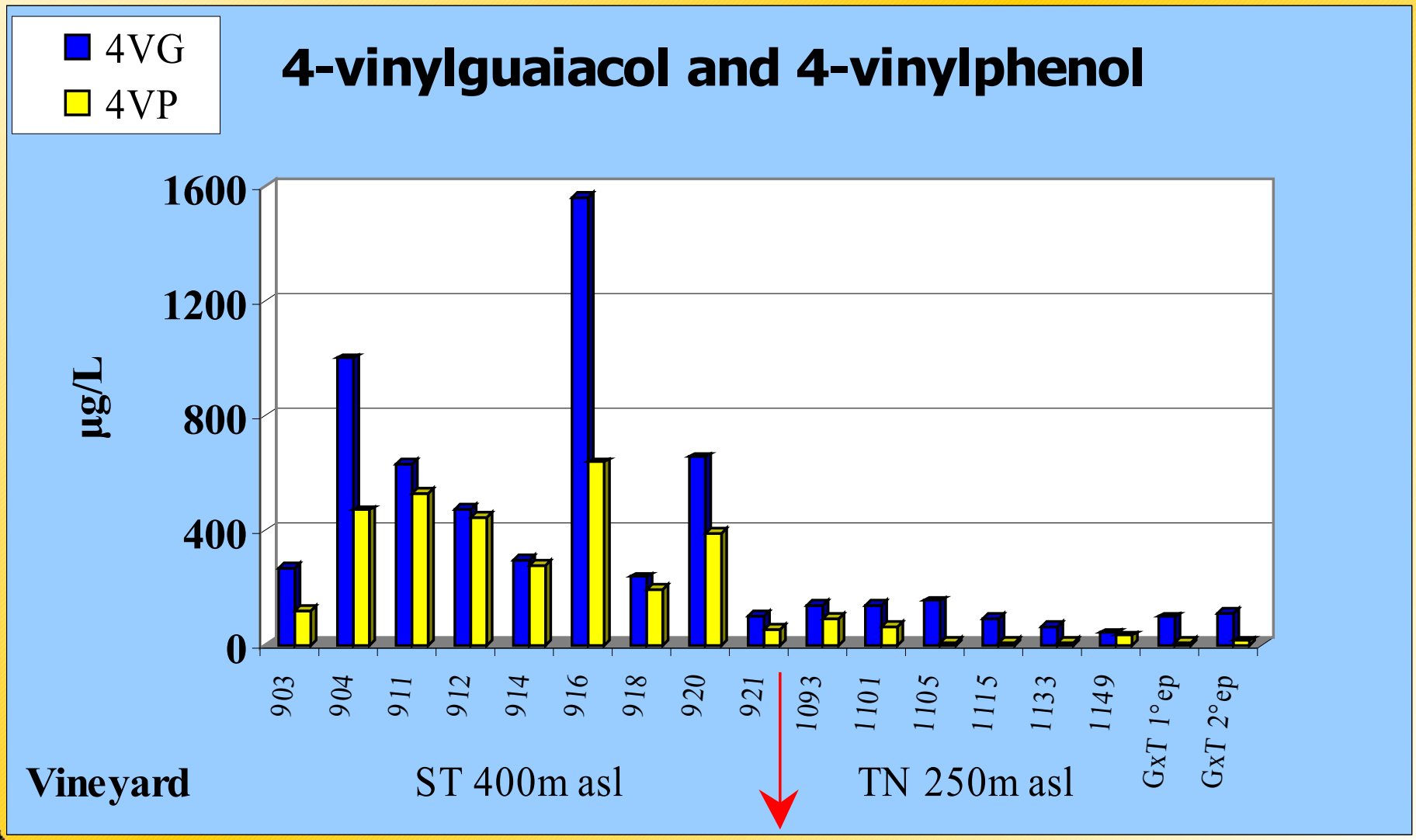

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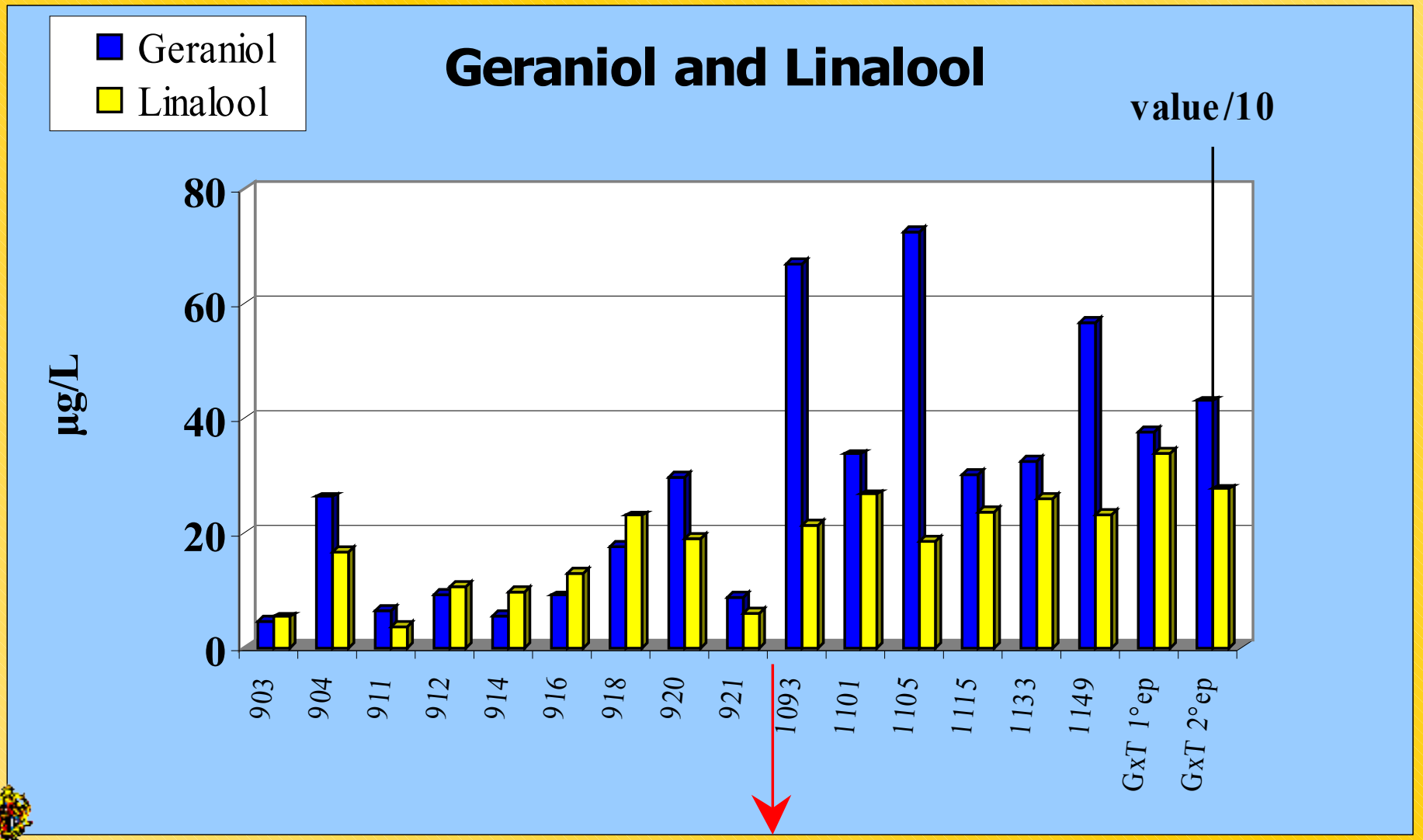

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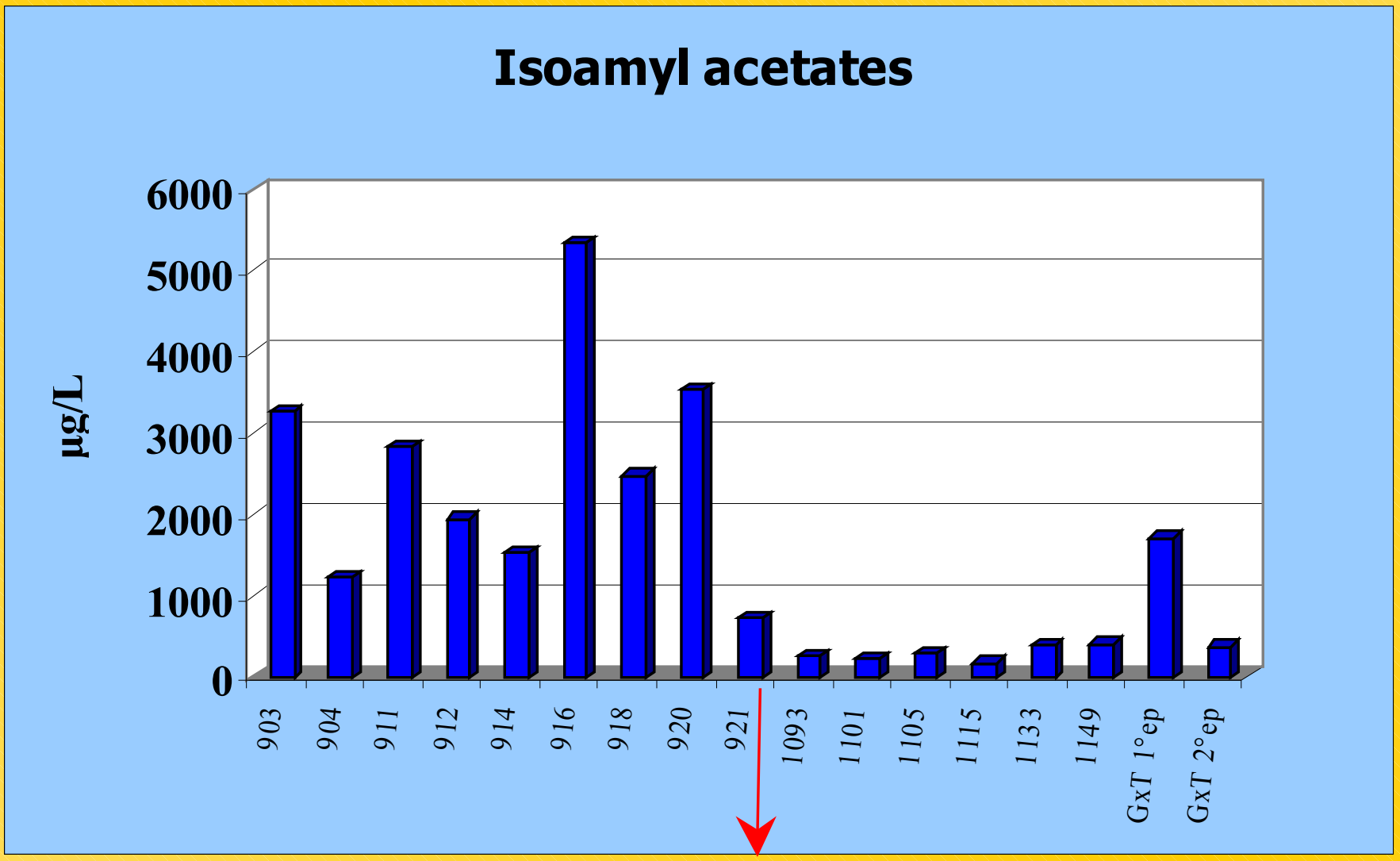
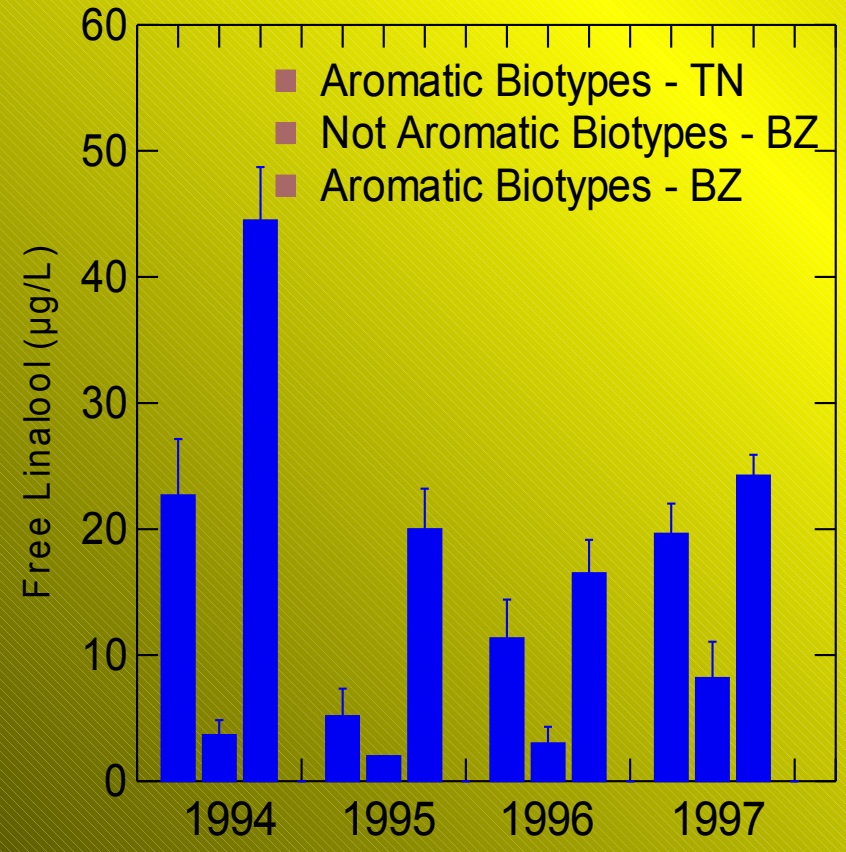
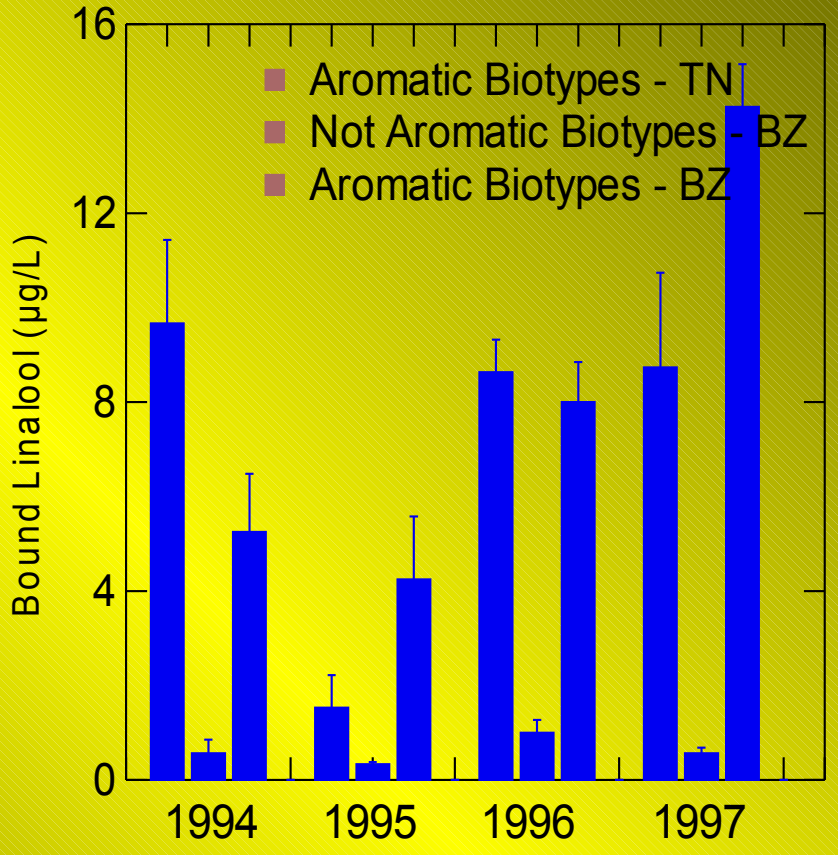
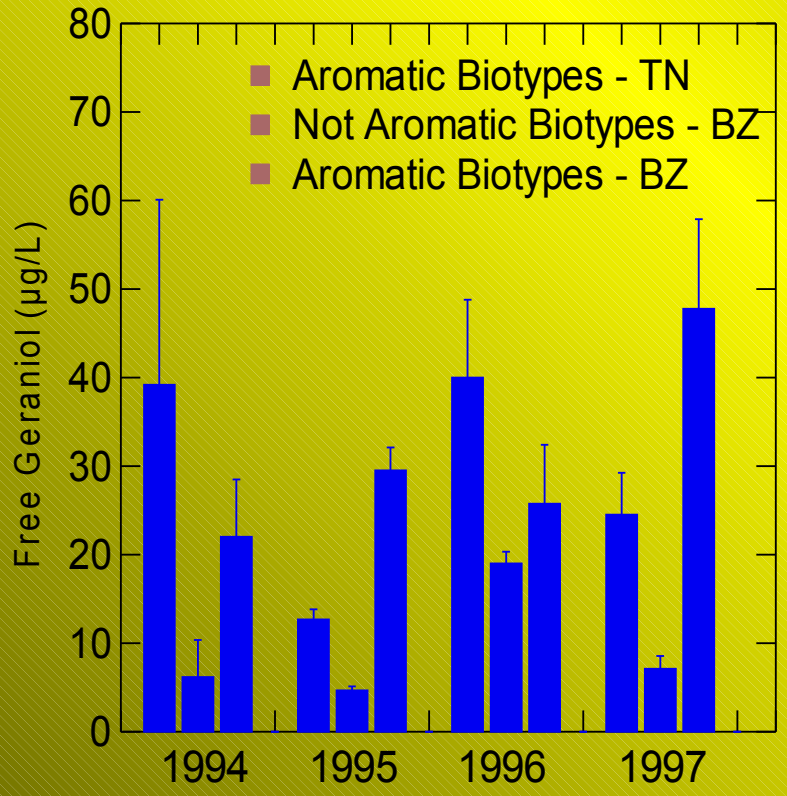


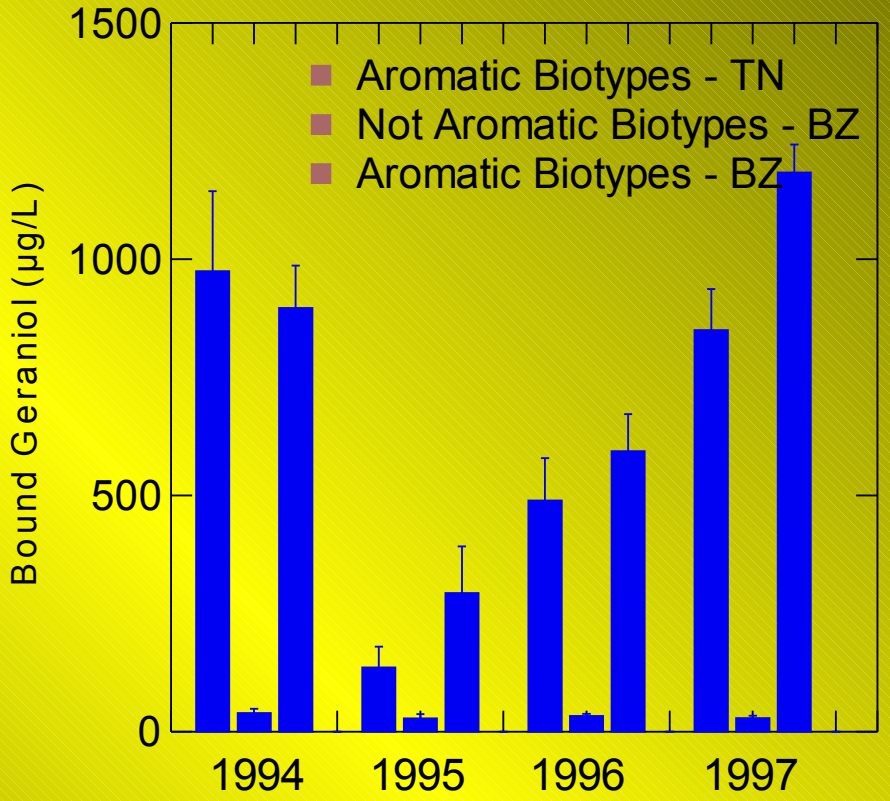
Traminer clonal wines:
variation of free and bound linalool by vintages



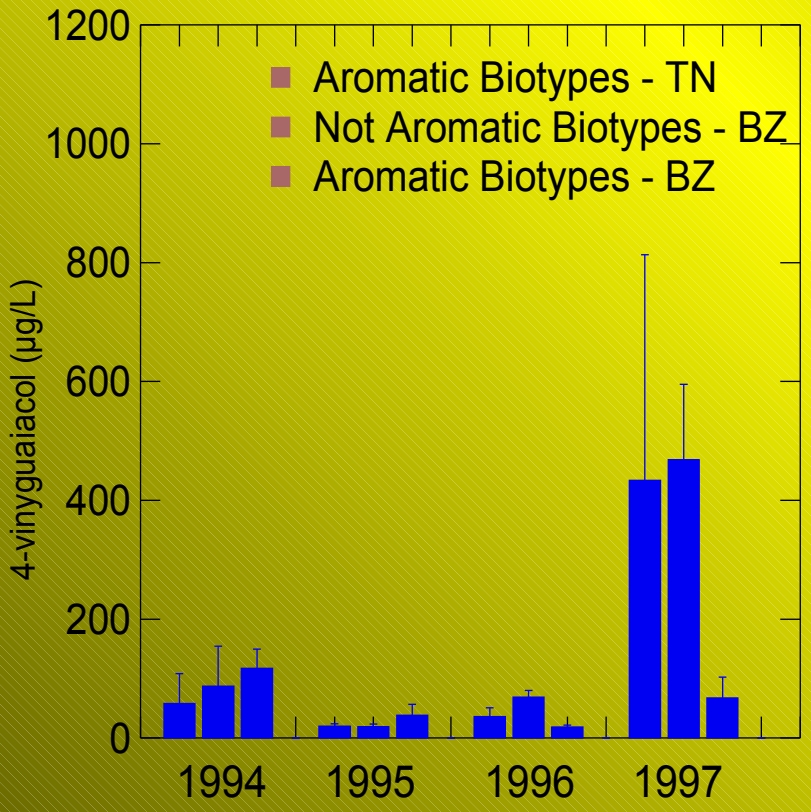


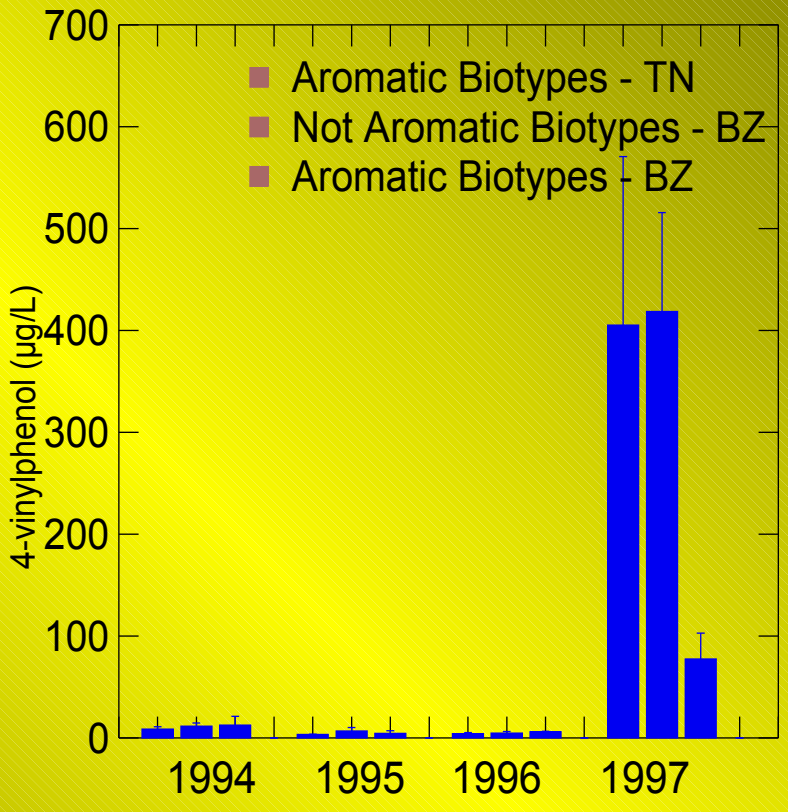
Traminer clonal wines:
variation of free and bound geraniol by vintages





Traminer clonal wines:
variation of volatile phenols by vintages





Comparison among wines of different vintages from Hungarian cultivars grown in Italy (Trentino) and in Hungarian regions: *varietal free compounds (µg/l)*

CULTIVAR	LEANYKA			HARSLEVELU			FURMINT			JUHFARK
REGION	EGER	IASMA	IASMA	EGER	IASMA	IASMA	PEC'S	IASMA	IASMA	BADACSONY
VINTAGE YEAR	'96	'95	'96	'96	'95	'96	'96	'94	'95	'96
cis furan linalool oxide	1,4	0,9	9,1	5,5	14	3,0	0,9	3,3	4,8	0,2
trans pyran linalool oxide	2,9	3,7	5,4	10	11	7,6	1,2	6,2	7,9	0,6
cis pyran linalool oxide	2,9	3,8	4,5	6,2	14	6,1	9,1	2,1	6,3	0,9
linalool	33	20	18	54	15	13	5,8	2,5	1,5	0,9
alpha-terpineol	3,3	13	14	13	14	9,1	1,2	8,3	7,9	0,9
citronellol	1,0	4,1	4,5	5,0	2,0	3,0	2,9	4,2	1,2	1,5
nerol	4,8	5,5	9,1	3,4	9,5	9,3	4,6	5,3	5,2	6,1
geraniol	11,5	11	16	20	11,5	11	6,1	10	6,0	2,3
Ho - dienol (i)	57	49	21	191	166	42	40	13	9,7	33
Ho - dienol (ii)	n.d.	26	9,0	10	40	7,0	1,8	3,0	2,4	4,8
hexanol	*1065*	*1529*	*3033*	*3014*	*1773*	*3270*	*1517*	*2909*	*980*	*569*
trans 3 - hexen-1-ol	28	66	49	44	25	81	59	111	4,5	6,5
cis 3 -hexen-1-ol	10	141	21	489	1268	739	38	1261	318	173
benzyl alcohol	13	32	7,7	120	9,9	22	106	22	18	43
2-phenylethanol	15666	24689	12531	101691	46591	50897	97264	25216	34696	27555

n.d. = not detectable

A. Dalla Serra et al., 2000. Proceed. Intern. Conference on: “Perspectives for horticulture and viticulture in the alpine region in the third millenium” pp. 247-252.

In *South Tyrol*, Pinot blanc cultivation area in 2004:

✓ha. 480 corresponding to hl 35.500 of wine,

10 % of the total wine production and one of the three most important white varieties (Chardonnay and Pinot gris) with similar winegrowing areas.

In *Trentino*, Pinot blanc with about 1% of the total wine production, is not so important in respect to Chardonnay (22%), the leading white variety, and Pinot gris (17%), the second white followed by Müller-Thurgau.

		PINOT BLANC				PINOT GRIS			
		North Italy		Germany		North Italy		Germany	
Compounds		x (24)	s	x (18)	s	x (10)	s	x (10)	s
ethanol	(% vol.)	11.33	1.15	12.89	1.07	12.25	0.70	13.27	1.33
methanol	(mg/l ass.)	19.7	5.8	37.8	5.9	27.0	4.0	41.4	10.4
1-propanol	"	15.9	10.6	28.3	10.0	29.1	22.6	28.9	16.3
2-methyl-1-propanol	"	28.8	11.6	76.9	32.2	45.1	25.3	77.6	35.5
2-methyl-1-butanol	"	28.1	9.3	42.6	21.3	28.2	9.6	45.4	23.0
3-methyl-1-butanol	"	151	35.7	178	106	145	31.1	171	84.0
higher alcohols	"	224	45.6	313	111	247	53.4	323	116
acetaldehyde	"	31.8	25.6	15.7	14.0	55.5	40.5	26.3	26.8
ethyl acetate	"	19.3	14.9	24.8	5.8	50.0	31.3	27.3	8.2
isoamyl acetate	(ug/L)	936	849	1532	566	1352	786	1421	353
ethyl caproate	"	475	216	399	126	412	118	346	140
ethyl caprylate	"	564	275	485	122	501	129	391	144
1-hexanol	"	2036	623	2639	399	2566	370	2406	770
trans 3-hexen-1-ol	"	71.7	39.8	43.1	7.7	150	109	44.1	16.9
cis 3-hexen-1-ol	"	52.5	34.5	101.0	30.2	42.8	20.2	66.3	24.0
phenethyl alcohol	"	42235	16563	54071	32225	31848	12275	60722	35527
N(isoamyl)-acetamid	"	211	382	5880	3143	1228	1586	4952	2494
4-vinylphenol	"	38.7	73.0	316	215	69.0	137	299	230
4-vinylguaiacol	"	11.5	13.4	65.4	36.8	19.1	12.9	44.8	32.1
linalool	"	2.9	2.7	22.5	16.2	3.8	2.2	17.4	13.1
alfa-terpineol	"	3.2	1.9	15.5	9.9	4.9	4.2	15.1	6.8
geraniol	"	2.9	2.5	11.2	6.4	3.6	1.9	9.7	5.6

Comparison of volatiles in Pinot blanc and Pinot gris wines from North Italy (Trentino-South Tyrol) and Germany (Palatinate)

COMPOUNDS	PINOT BLANC (24)		PINOT GRIS (10)	
	MEAN VALUE	STD DEV	MEAN VALUE	STD DEV
TRANS FURAN LINALOOL OXIDE	1.91	1.718	2.28	2.287
CIS FURAN LINALOOL OXIDE	1.14	0.799	1.56	0.923
LINALOOL	0.24	0.489	0.27	0.299
α -TERPINEOL	2.29	1.708	4.61	1.397
TRANS PYRAN LINALOOL OXIDE	0.59	0.557	0.93	0.850
CIS PYRAN LINALOOL OXIDE	0.37	0.287	0.43	0.390
CITRONELLOL	0.18	0.105	0.22	0.147
NEROL	1.24	0.560	1.51	0.451
GERANIOL	4.71	1.831	6.12	3.019
TRANS GERANIC ACID	4.54	3.986	3.57	1.176
HO-DIENDIOL (I)	2.38	1.775	2.35	1.466
TRANS 8-OH-LINALOOL	9.10	3.494	14.2	5.02
CIS 8-OH-LINALOOL	21.1	10.45	22.4	13.25
3-OXO-α -IONOL	228.5	66.09	210.1	35.38
2-EXO-OH-1,8-CINEOL	0.62	0.471	0.94	0.409
7-OH-GERANIOL	2.87	2.505	5.18	3.868
8-OH-GERANIOL	22.9	9.84	42.1	49.50
P-MENTH-1-EN-7,8-DIOL	13.6	7.72	15.6	4.47
BENZYL ALCOHOL	75.2	36.75	80.2	26.00
PHENETHYL ALCOHOL	138.8	90.80	130.1	89.25

Tab. 10: Bound compounds (μg/L) in Italian Pinot Blanc and Pinot Gris wines.

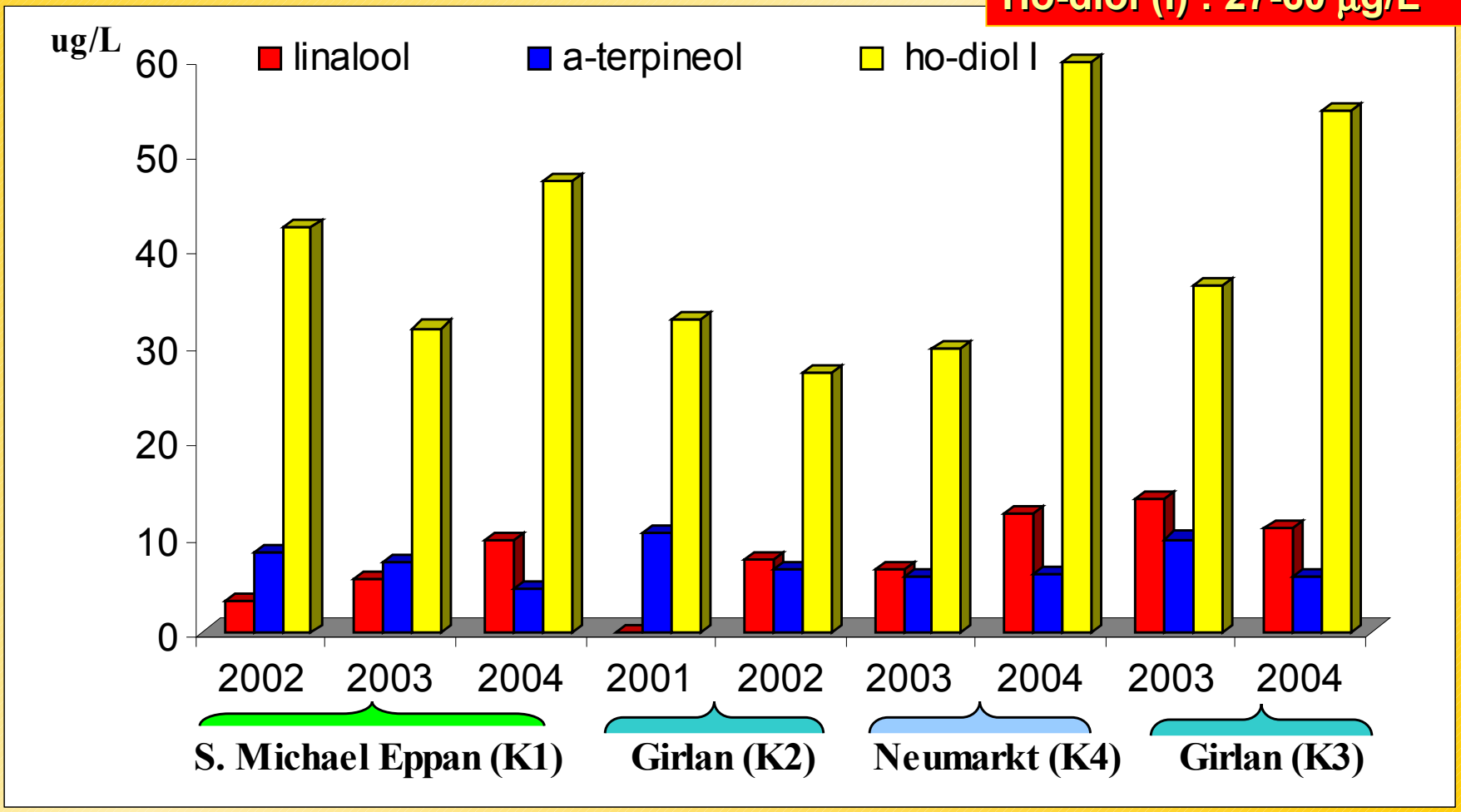
COMPOUNDS	PINOT BLANC		PINOT GRIS	
	MEAN VALUE (8)	MEAN VALUE (2)	MEAN VALUE (7)	MEAN VALUE (3)
TRANS FURAN LINALOOL OXIDE	12.5	51.7	14.0	15.6
CIS FURAN LINALOOL OXIDE	11.1	71.3	11.4	11.0
LINALOOL	3.18	7.00	3.46	3.60
α -TERPINEOL	12.9	14.3	15.4	10.9
TRANS PYRAN LINALOOL OXIDE	4.62	25.3	5.68	6.23
CIS PYRAN LINALOOL OXIDE	2.17	8.55	4.00	2.30
CITRONELLOL	0.24	4.15	0.41	0.37
NEROL	5.90	53.8	6.20	6.20
GERANIOL	18.4	95.7	19.3	16.5
TRANS GERANIC ACID	14.3	97.6	11.3	19.2
HO-DIENDIOL (1)	8.91	31.4	15.8	12.2
TRANS 8-OH-LINALOOL	25.6	102.4	29.3	39.7
CIS 8-OH-LINALOOL	36.7	125.7	38.1	58.3
3-OXO-α -IONOL	316.9	322.0	325.0	282.0
2-EXO-OH-1,8-CINEOL	1.59	3.00	3.26	3.70
7-OH-GERANIOL	14.4	53.1	18.3	14.7
8-OH-GERANIOL	42.7	70.0	46.5	64.0
P-MENTH-1-EN-7,8-DIOL	9.84	25.6	22.3	18.4
BENZYL ALCOHOL	111.4	128.0	160.7	146.7
PHENETHYL ALCOHOL	146.6	487.5	200.6	290.7

Tab. 12: Bound compounds (μg/L) in German Pinot Blanc and Pinot Gris wines. The wines of one winery (1) are reported separately.

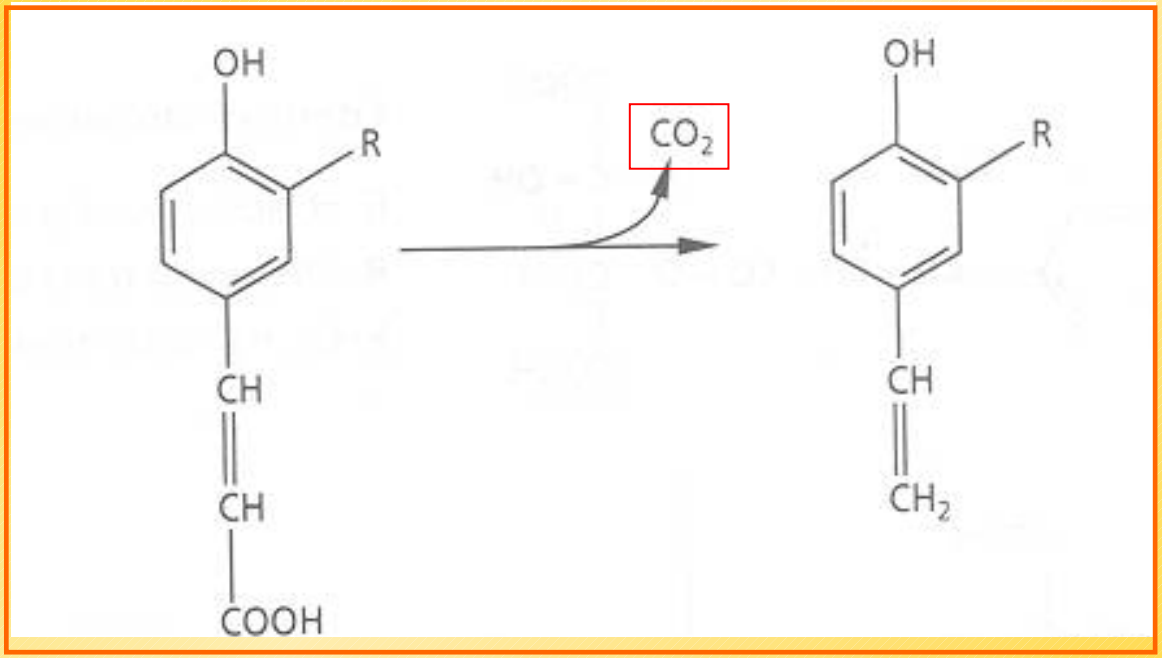
South Tyrolean Pinot blanc wines: level of some monoterpenols (GC-MS) *(recent analyses)*

L + a-T: 10-23 µg/L

Ho-diol (l) : 27-60 µg/L



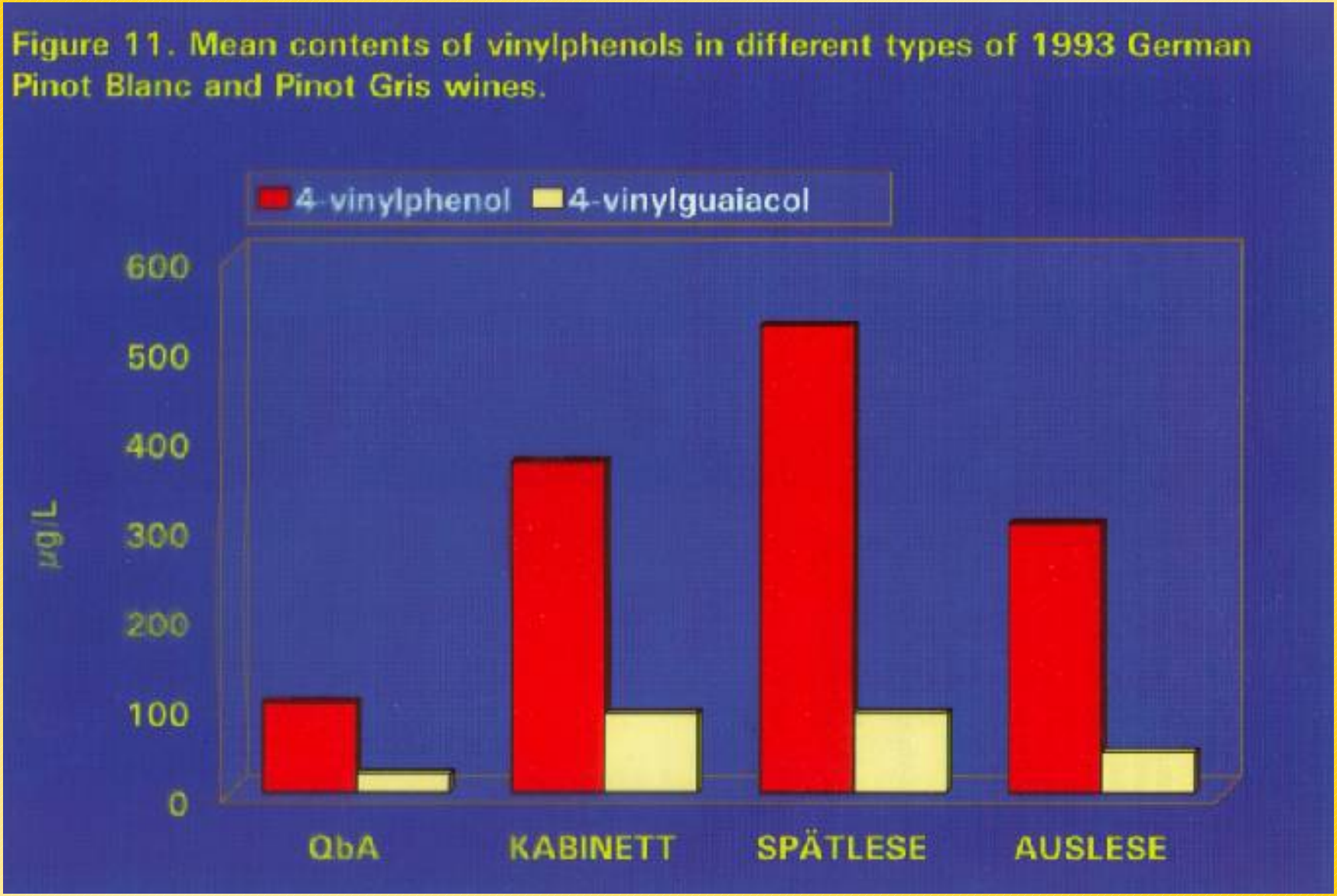
Biosynthesis of vinylphenols from free relevant cinnamic acids by POF(+) yeasts



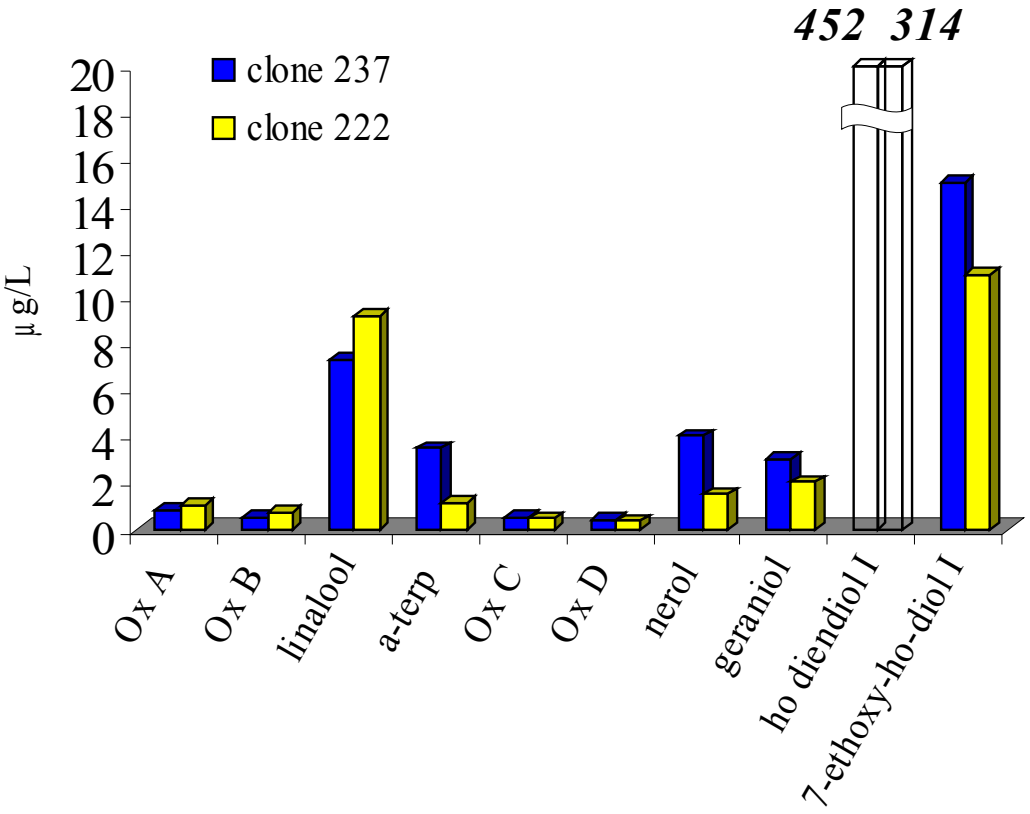
R = H: p-cumaric acid
R = OCH_3: ferulic acid

R = H: 4-vinylphenol
R = OCH_3: 4-vinylguaiacol

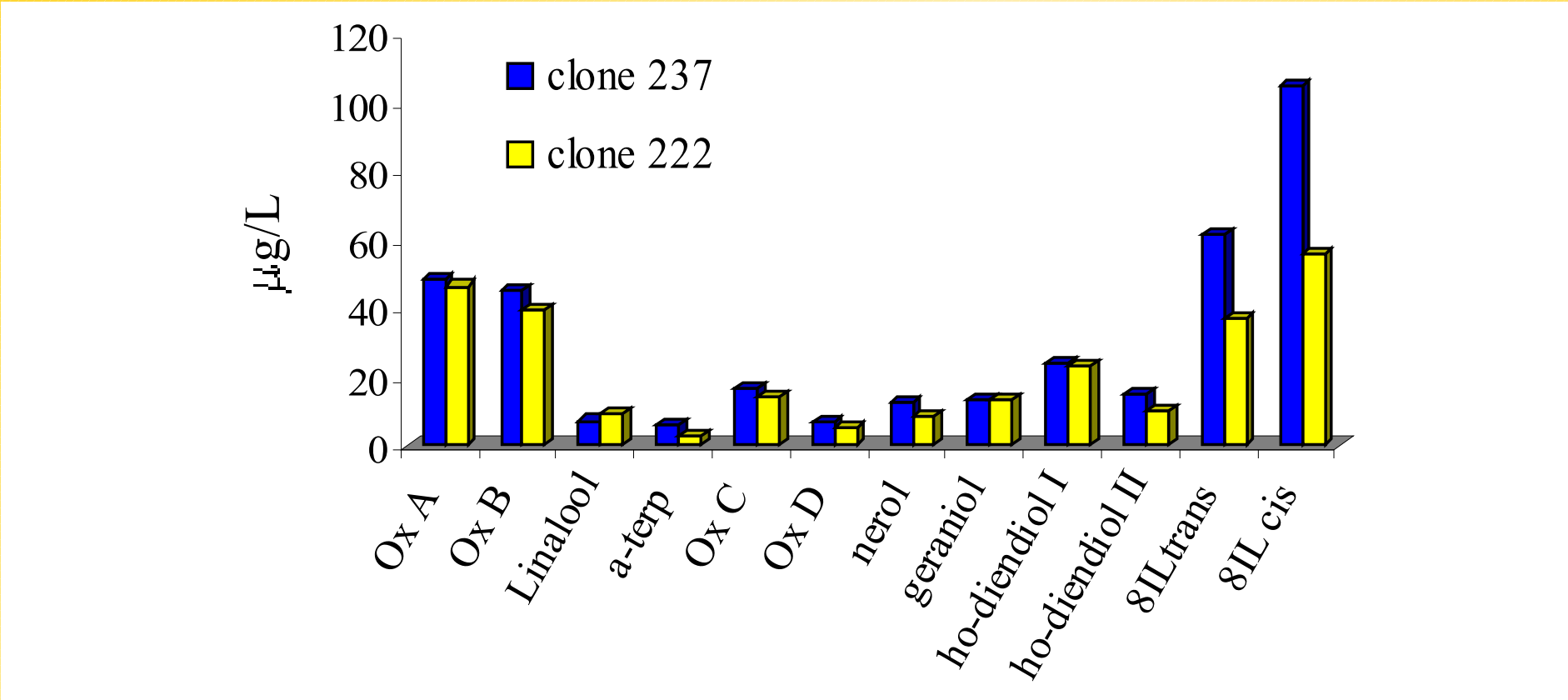
Figure 11. Mean contents of vinylphenols in different types of 1993 German Pinot Blanc and Pinot Gris wines.



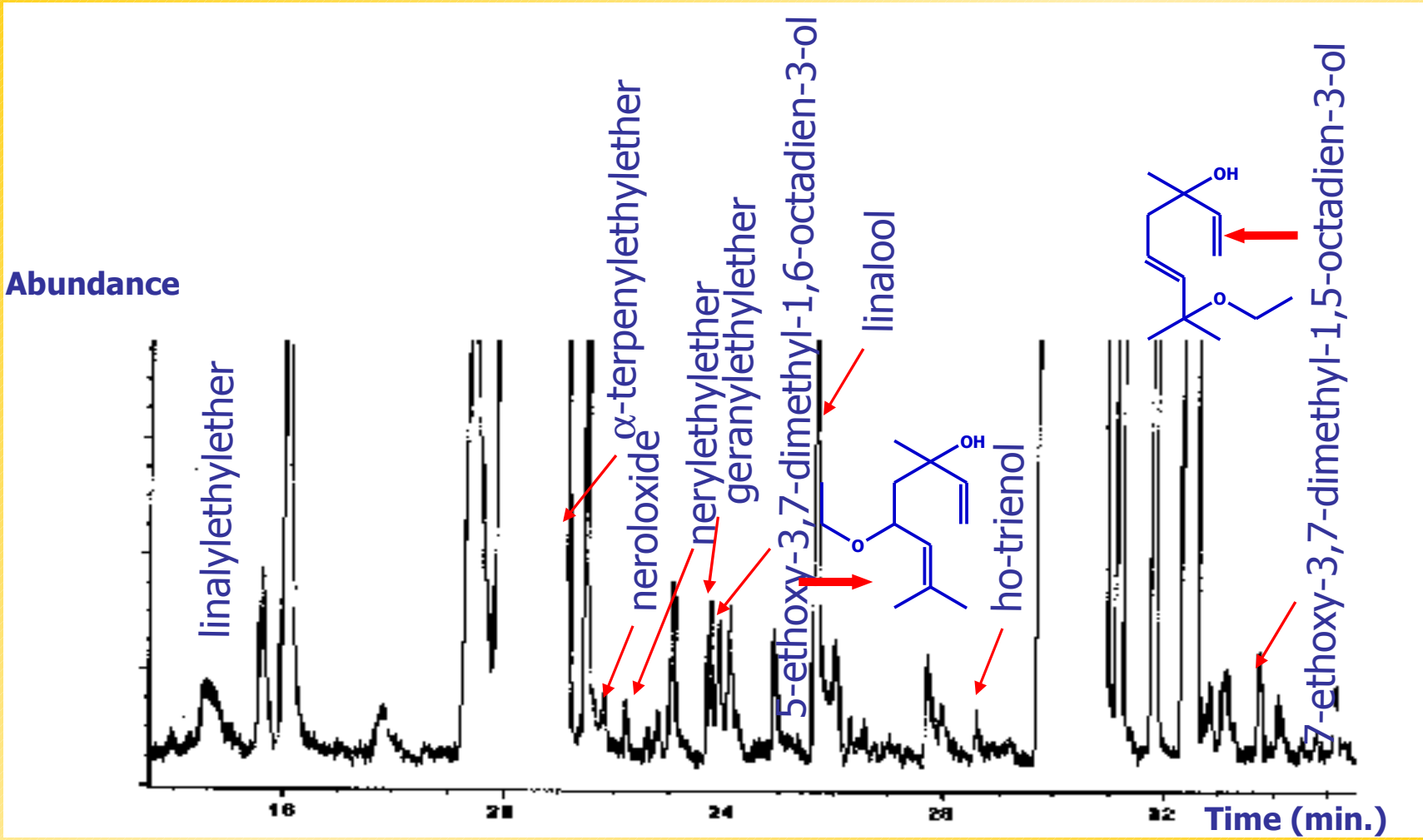
Example of free monoterpenes profile of 2000 “Manzoni bianco” IM 6-0-13 clonal wines (Telve V.S., Trentino; 400 m asl)



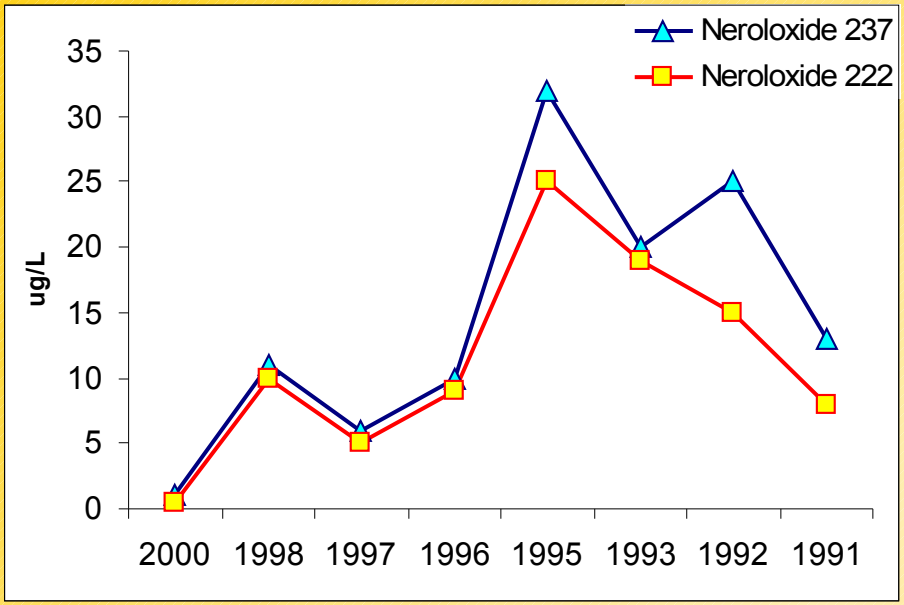
Example of bound monoterpenes profile of 2000 “Manzoni bianco” IM 6-0-13 clonal wines (Telve V.S., Trentino; 400 m asl)

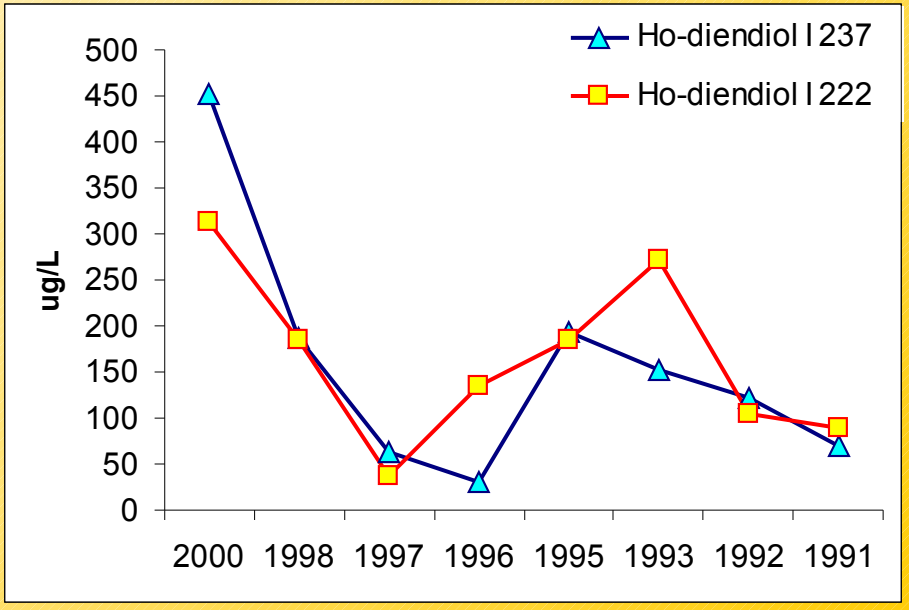


Partial SPME-GC-TIC chromatogram showing the position of some monoterpenes and monoterpenes ethers (1998 Müller-Thurgau wine)



Evolution of some monoterpenes during the ageing of Manzoni bianco" wines

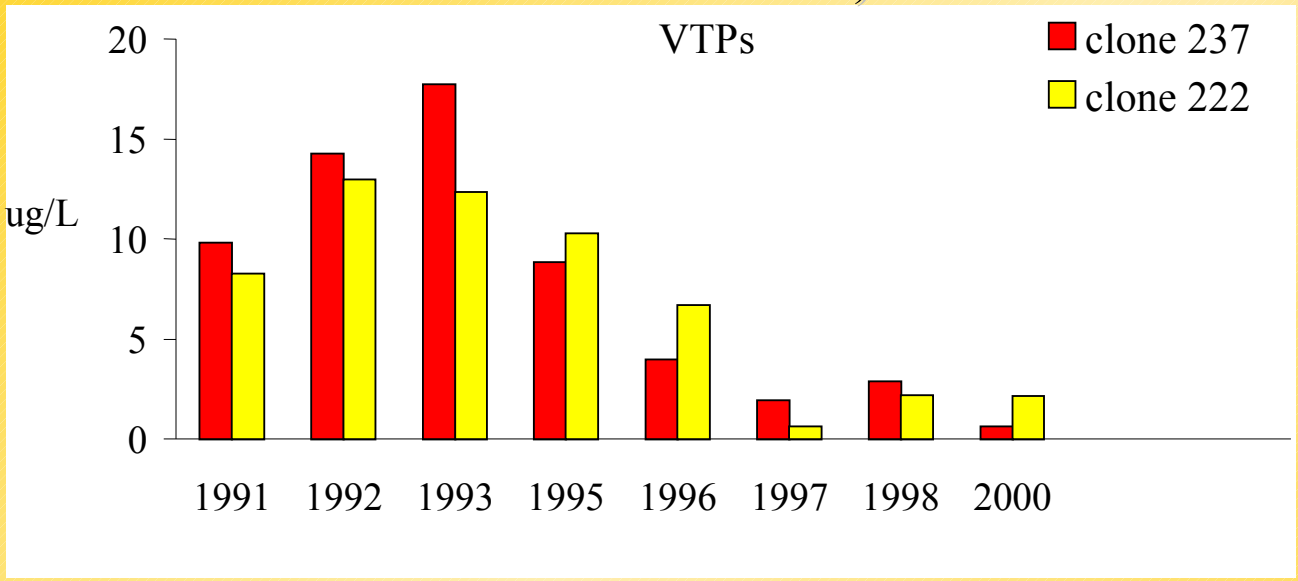


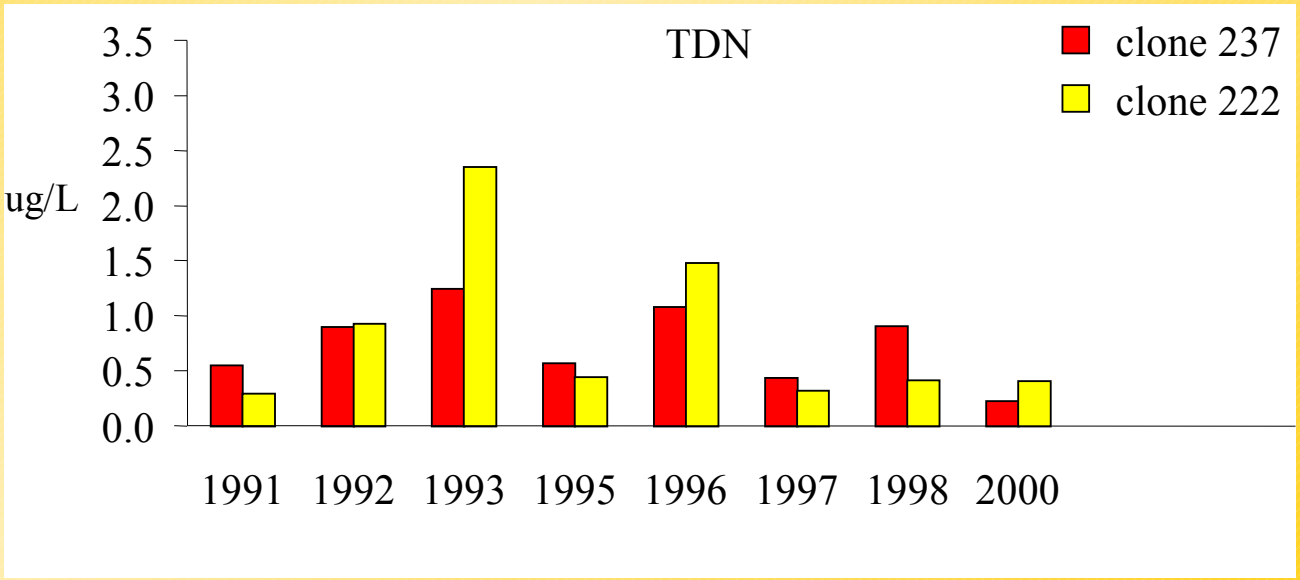


Wine-growing areas:

Telve 400 m asl: 1995-2000;
S Michele a/A 200m asl: 1993;
Gardolo 200 m asl: 1991-1992

TDN and VTPs level in differently aged "Manzoni bianco" wines of Trentino (Telve 400m asl: 1995-2000; S Michele a/A 200m asl: 1993; Gardolo 200 m asl: 1991-1992)





Evolution during the ageing of "Manzoni bianco" wines, usually at a rather low pH value around 3.0:

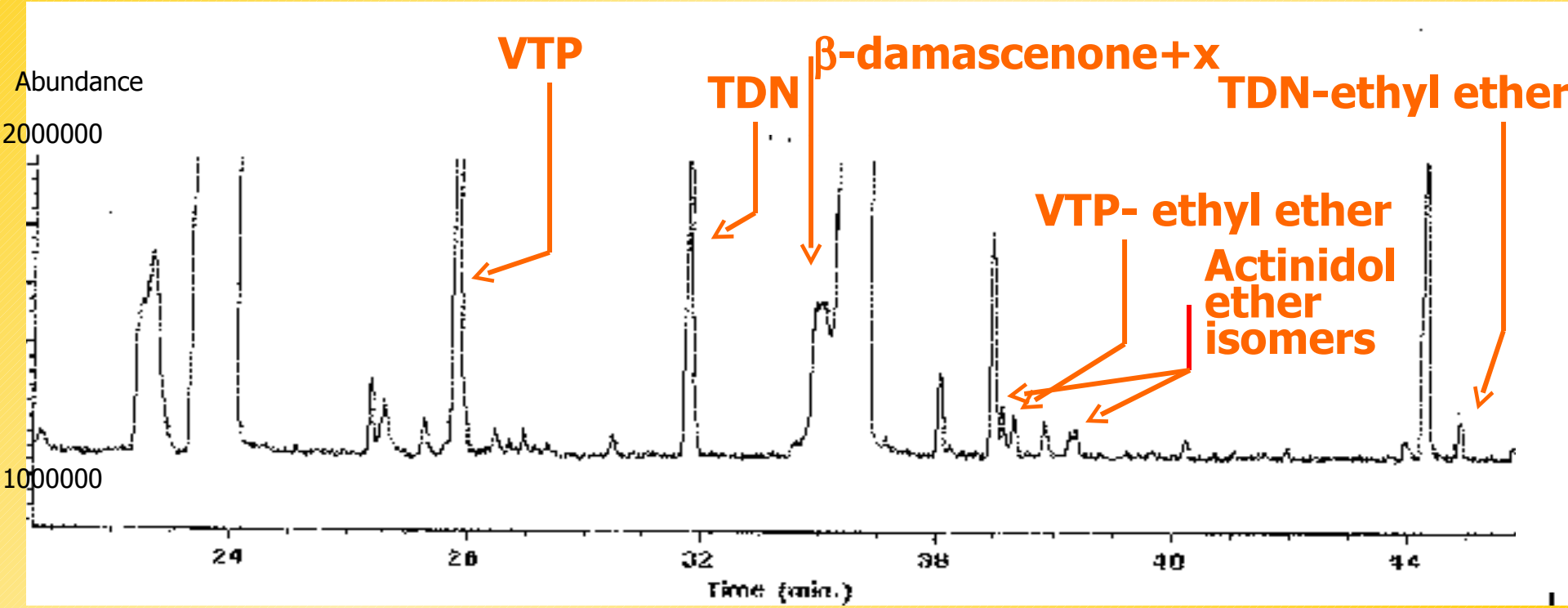
⇨ rapid decrease of diol ethyl ethers;

⇨ possible aroma contribution of neroloxide only after 4-5 years;

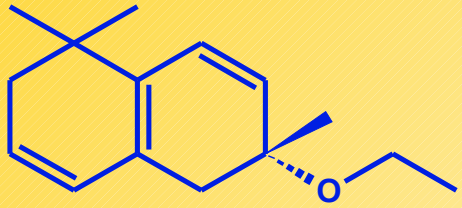
⇨ no interesting increase of ho-trienol except in some aged samples (real content by HS/SPME-GC analysis); α-terpineol is not higher than 10 µg/L; the level of 1,8-terpin is rather low;

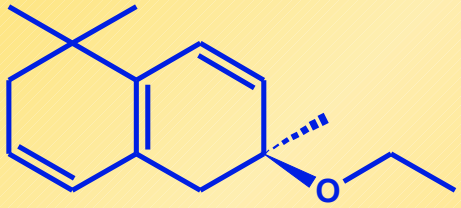
⇨ increase of TDN (max 2.5 µg/L), vitispiranes (VTP: max 18 µg/L) and actinidols as shown in Figure (no significant differences in wines of Sicily) with increasing eucalyptus/balsamic-resinous/woody-like scent: possible contribution to the aroma by ethyl ethers of TDN and VTP "precursors" and of actinidols.

Partial TIC-chromatogram showing the relative positions of some norisoprenoids (cap.column:PS 264)

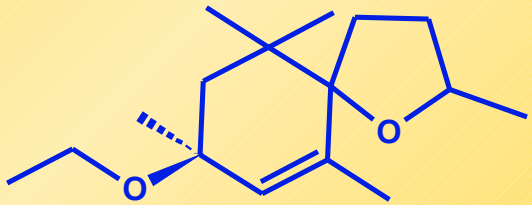


Structures of ethoxy-derivatives of TDN, VTP and actinidols

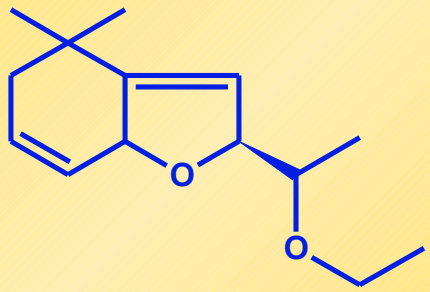


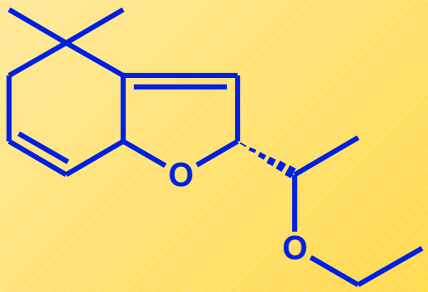


ethoxy-TDN



ethoxy-VTP





ethoxy-actinidols

Müller-Thurgau

Aroma profile of free and bound forms in Müller-Thurgau floral wines from Trentino (different clones and vintages) with a floral, a little Muscat, Riesling-like peach scenting aroma:

⇨ about 70-85% of linalool in musts as bound form: complete chemical hydrolysis usually within 6-8 months: formation of (R)- and (S)-linalool enantiomers;

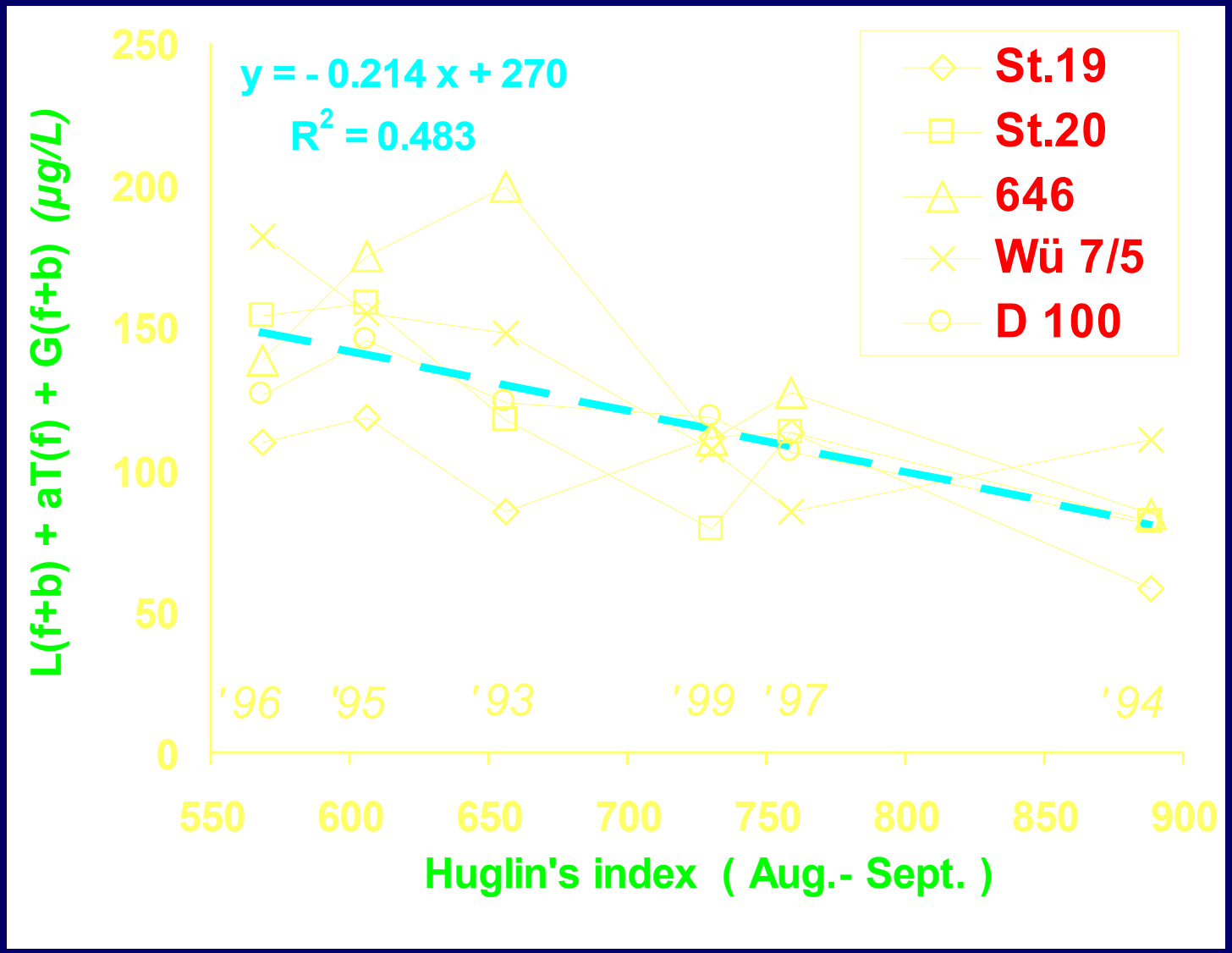
⇨ remarkable difference for linalool, but even more for hodiendiol (I) among different wine-growing areas.

Free and bound monoterpenols in 1995 Müller Thurgau musts from most important production areas of Trentino, referred to different grape ripening steps *(4-5 weekly samplings until overripening)*

FREE FORMS (µg/l)	mean (n=51)	st. dev.	min	max
trans furan linalool oxide	4.2	1.5	1.3	7.6
cis furan linalool oxide	1.4	0.5	0.6	3.0
linalool	***15.8***	***8.5***	***4.2***	***35.2***
α -terpineol	3.6	2.4	0.6	9.1
ho-diendiol (I) ethylether	28.1	14.2	10.4	78.0
trans pyran linalool oxide	29.9	18.8	5.3	95.9
cis pyran linalool oxide	2.5	0.9	0.9	5.1
citronellol	1.7	0.4	0.9	2.7
geraniol	2.5	1.8	0.5	10.3
ho-diendiol (I)	***403.9***	***171.9***	***136.3***	***765.0***

BOUND FORMS (µg/l)	mean (n=51)	st. dev.	min	max
trans furan linalool oxide	66.9	24.5	25.7	132.2
cis furan linalool oxide	6.8	2.2	2.1	11.9
linalool	***36.1***	***20.1***	***5.0***	***87.1***
α -terpineol	1.2	0.6	0.4	2.5
trans pyran linalool oxide	14.4	6.1	3.8	26.6
cis pyran linalool oxide	3.4	1.7	1.3	9.1
geraniol	14.5	4.1	7.4	24.2
ho-diendiol (I)	***79.1***	***38.8***	***22.4***	***200.6***
trans 8-hydroxylinalool	12.9	6.2	3.6	26.4
cis 8-hydroxylinalool	20.1	8.9	4.7	36.3

"Floral" aroma achievable in Müller-Thurgau clonal wines related to the Huglin's index over different years



Monoterpenes (mean, st. dev., µg/L) of 1998 Müller-Thurgau commercial wines from different Italian regions *(analysis in 1999)*

Compound	*Aosta Valley (n=3)*	*Friuli V.G. (n=4)*	*Trentino (n=3)*	*South Tyrol (n=3)*
free forms				
linalool	70±*16*	34±*13*	71±*3*	174±*53*
alpha-terpineol	24±*7*	15±*6*	32±*4*	42±*4*
geraniol	22±*10*	12±*9*	13±*7*	19±*4*
ho-diol (I) + trienol	122±*17*	87±*5*	247±*21*	390±*81*
bound forms				
t. fur. linalool ox.	19±*1.5*	18.5±*17*	19±*3.5*	40±*21*
c. fur. linalool ox.	10.5±*5.5*	7.5±*5*	9±*2*	8±*4*
linalool	34±*4*	19±*9*	11±*4*	28±*12*
geraniol	13.5±*3*	25±*15*	15±*4*	27±*15*
ho-diol (I) + trienol	38±5	28.5±*6*	43±*2*	46.5±*17*
cis 8-OH-linalool	22±*7.5*	39±*23*	24±*4*	19±*4*

Variability of (S)-enantiomeric linalool in musts:

⇨ as free form: for Rhine Riesling and its crosses Scheurebe, Müller-Thurgau from 94 to 98%; for Ehrenfelser and Kerner from 70 to 80%;

⇨ as bound form: for all quoted varieties: from 90 to 97%.

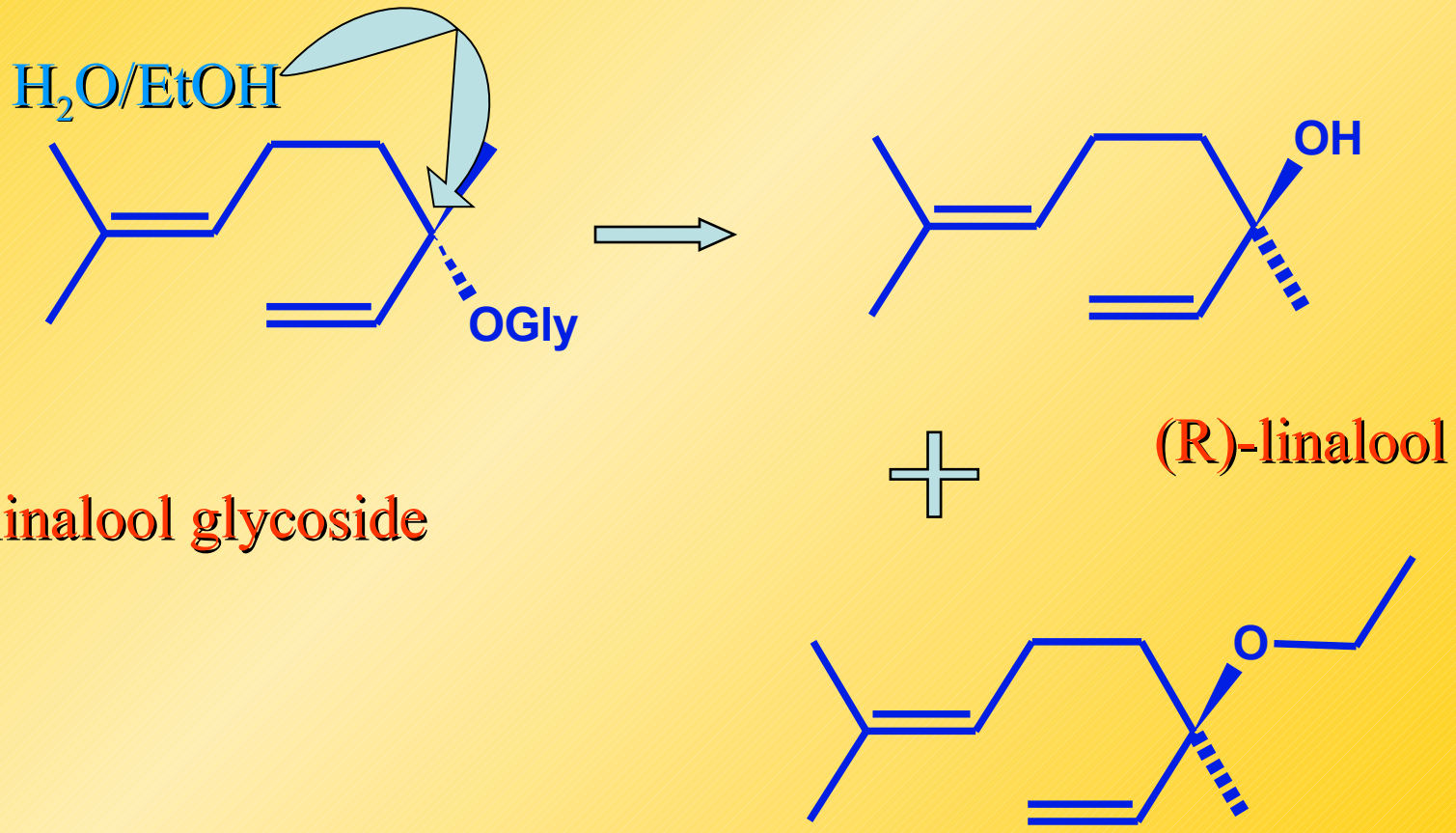
(tendency according to Doglia, 1993; Garcia-Moruno, 1999 & Luan et al., 2004).

Examples of (S)-enantiomeric free linalool percentage variability in wines (analysis in 2005):

R.Riesling, Mosel, 2003:	43%;
R. Riesling IASMA, 2004:	44%;
IM 6-0-13 IASMA, 2004:	47%;
Yellow Muscat IASMA 2004:	88%.

(Versini et al., in submission to Vitis)

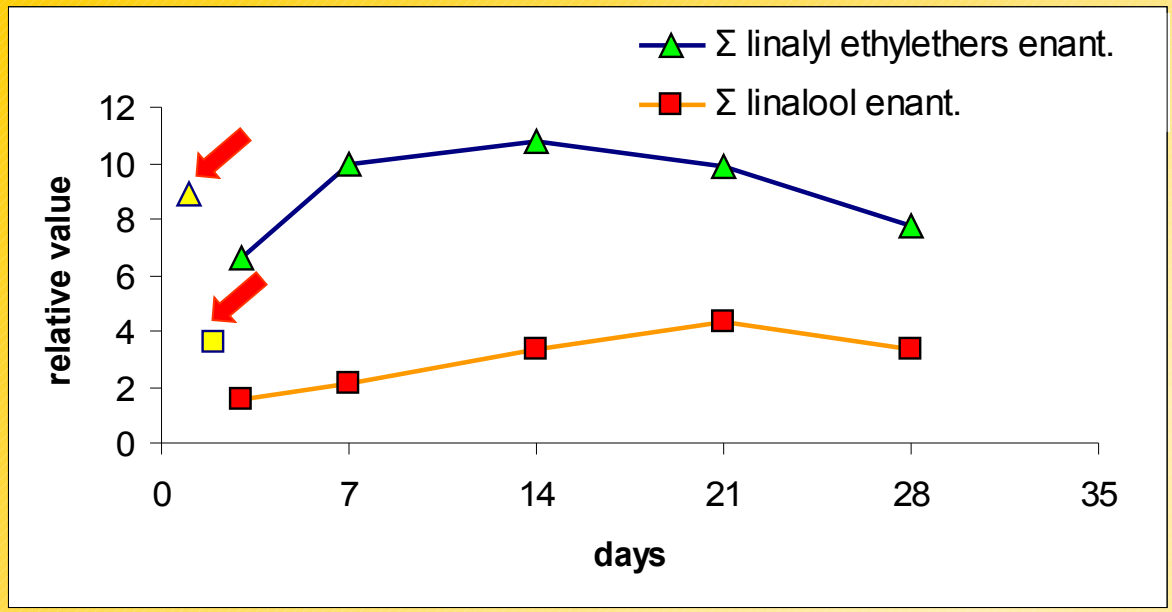
Prevalent stereospecific reaction mechanism of hydrolysis/ethanolysis of (R)/(S)-linalool glycosides



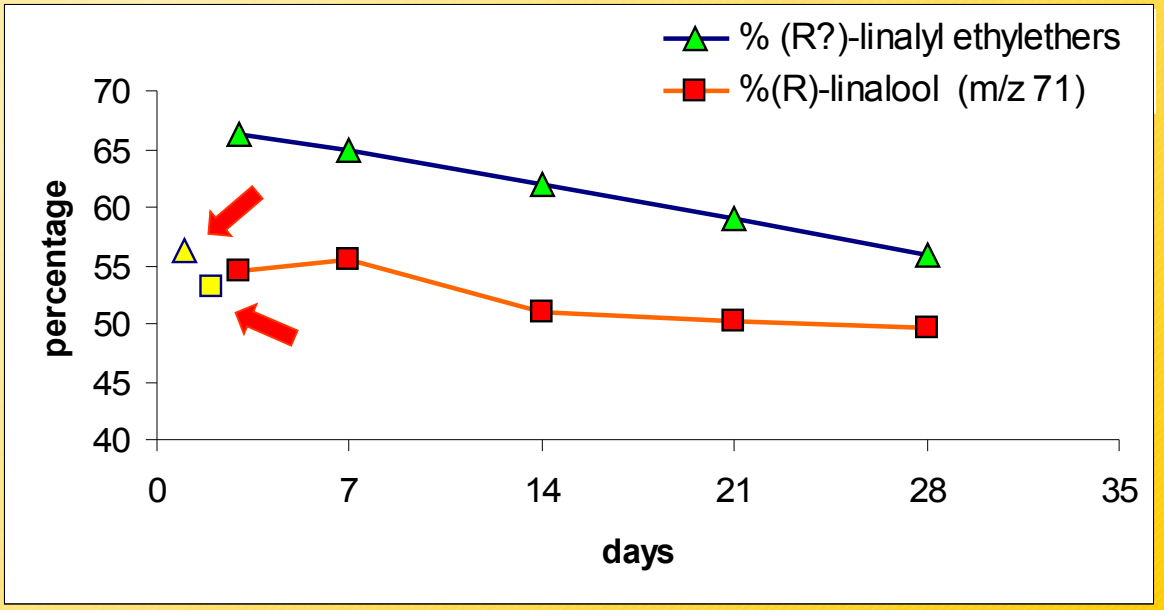
(S)-linalool glycoside

(R)-linalool

(R)-linalool ethylether *(traces)*

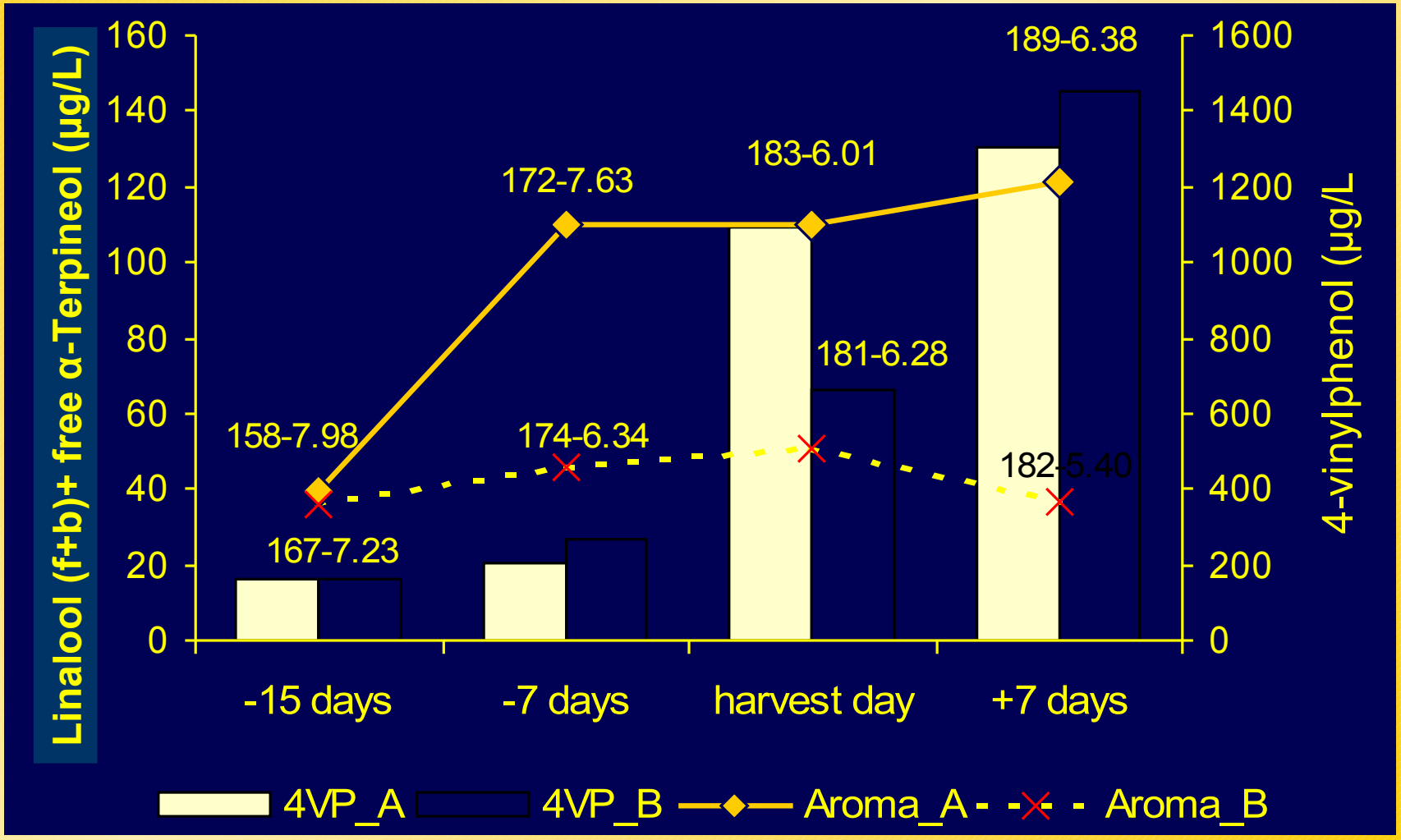


Kinetics of linalool and linalyl ethylether enantiomers formation from linalool bound form in a synthetic alcoholic solution (30°C, pH 3.2; 12 % vol):



Value indicated by a red arrow: level reached by speeded kinetics (3 days at 40°C)

Changes of Müller-Thurgau wine aroma compounds in relation to the grape ripeness (sugar-total acidity, g/L) in two vineyards (A, B) - vintage 1996



Conclusion:

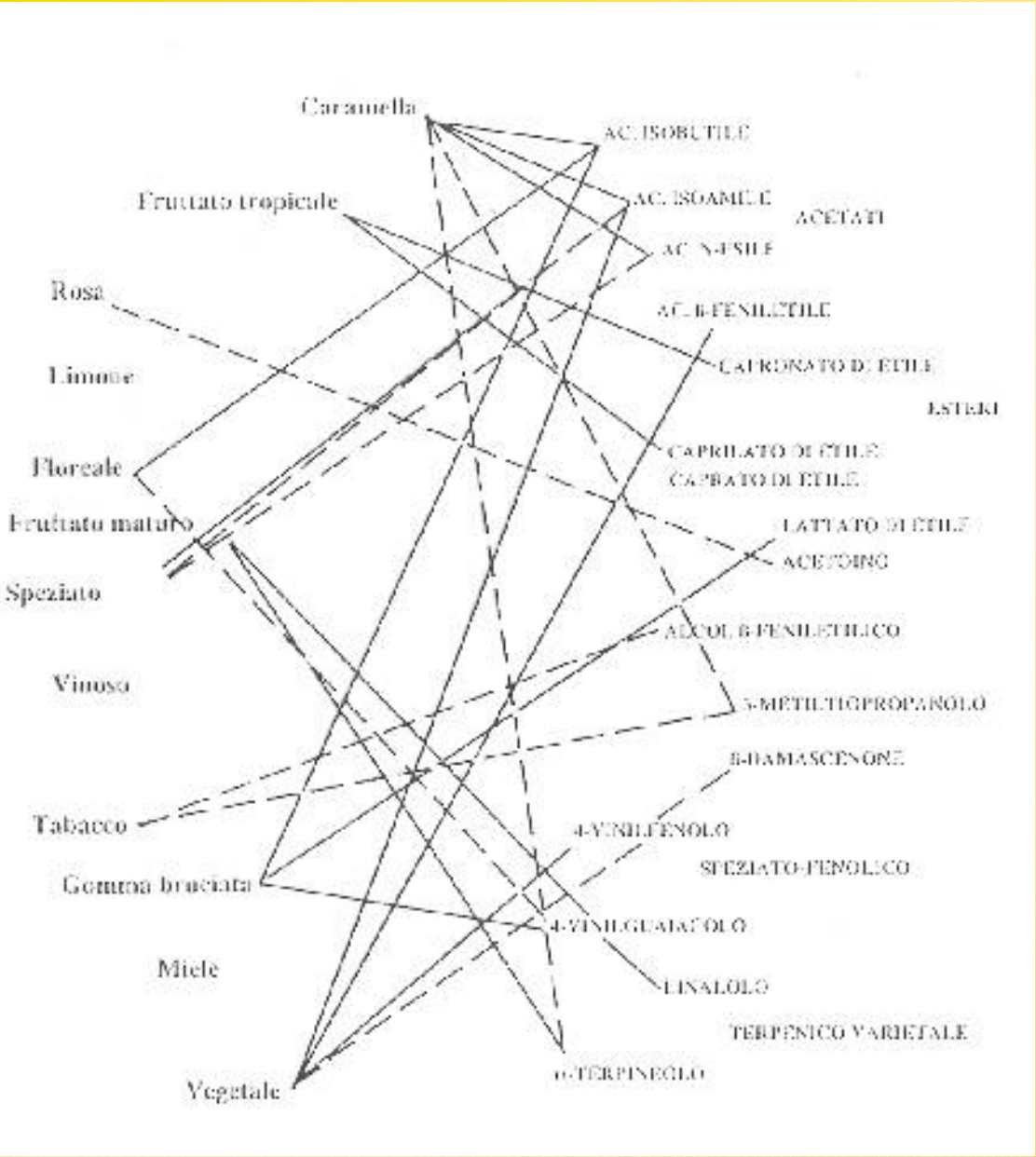
The hydrolysis of bound linalool form happens with a **dominant inversion** at about 70% of the configuration at C3 and this fact mostly determines the final level and peculiar (R)/(S) ratio of linalool in the wines.

Thus, the wines can show a prevalence of the peach-like/lavender-like/woody fragrance-like aroma associated to the (R)-form, while the (S)-form is mostly petitgrain/coriander oil-like scenting.
Rhine Riesling and several relevant crosses are likely for this reason not muscat-scenting.

Conclusion (2):

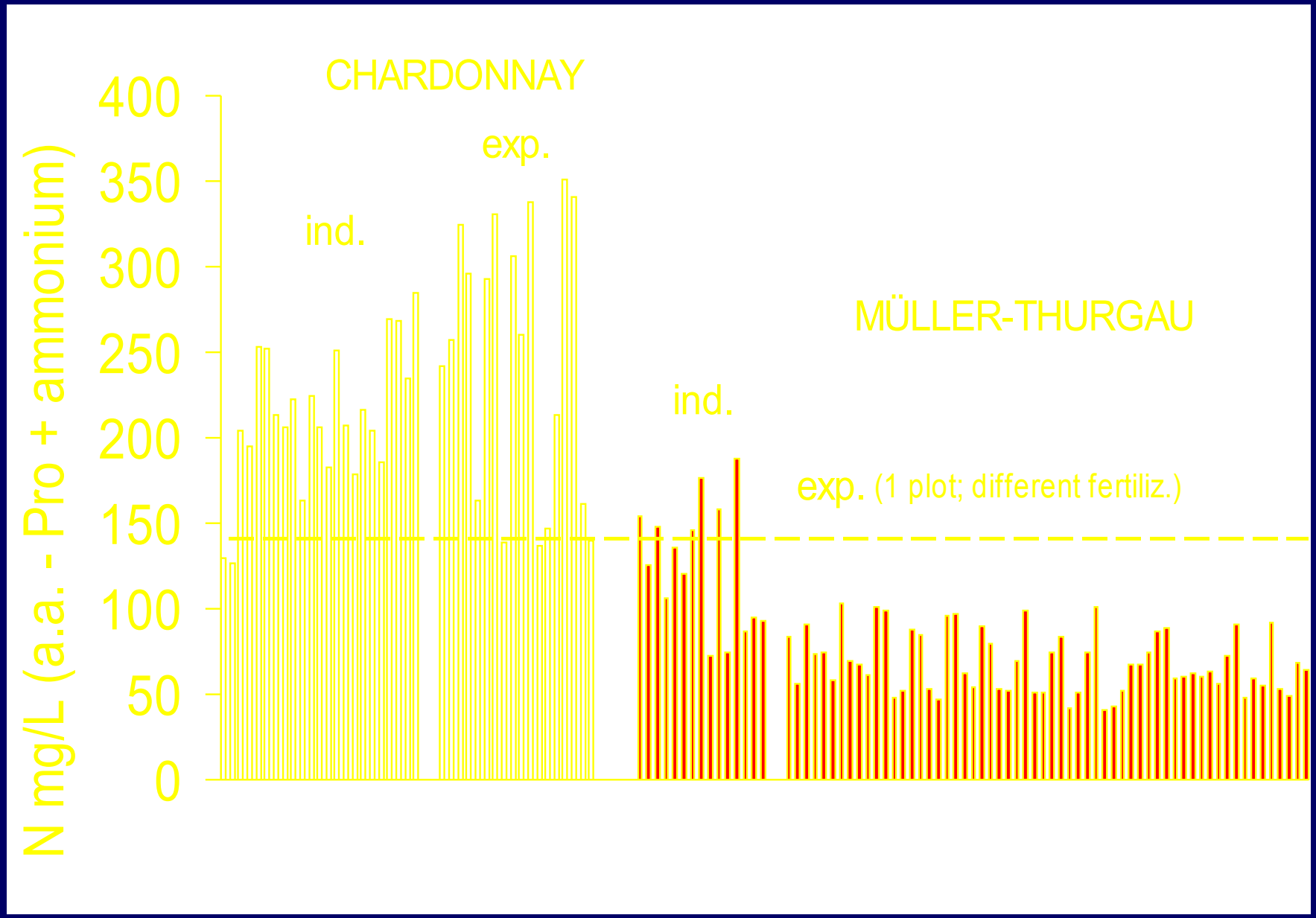
Depending on pH and storage temperature, roughly after about 3 years the racemisation of linalool is complete.

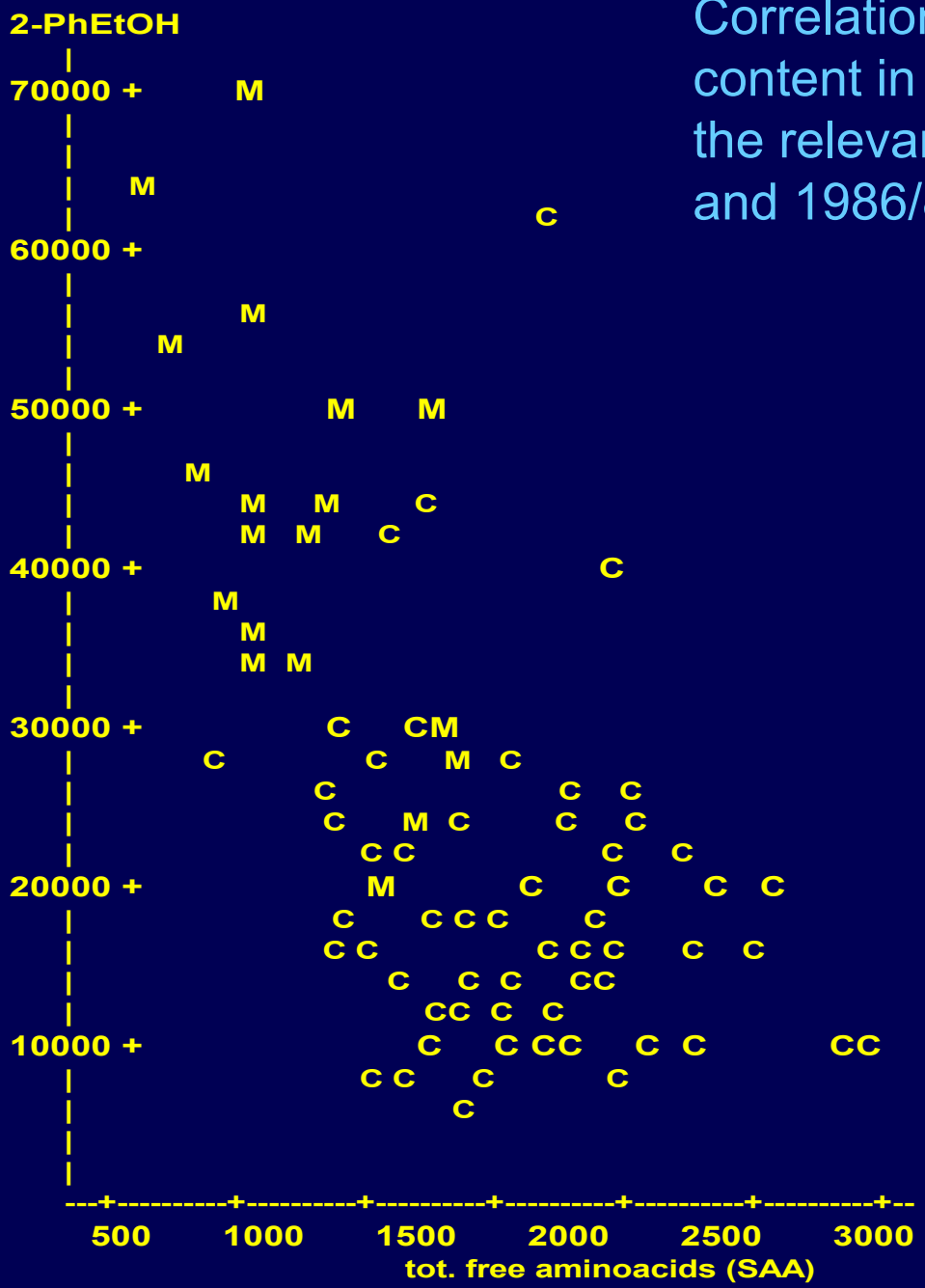
(R?)-likely linalyl ethylether remains for a longer time in its prevalent enantiomeric form both in Rhine Riesling and Muscat wines, this fact demonstrating the origin only from bound linalool.



1987 and '88 Chardonnay sparkling-base wines of Trentino (microvinification of 50 l): significant correlations between scents and volatile compounds levels *(Iacono et al, Riv. Vitic. Enol., 4, 1990)*

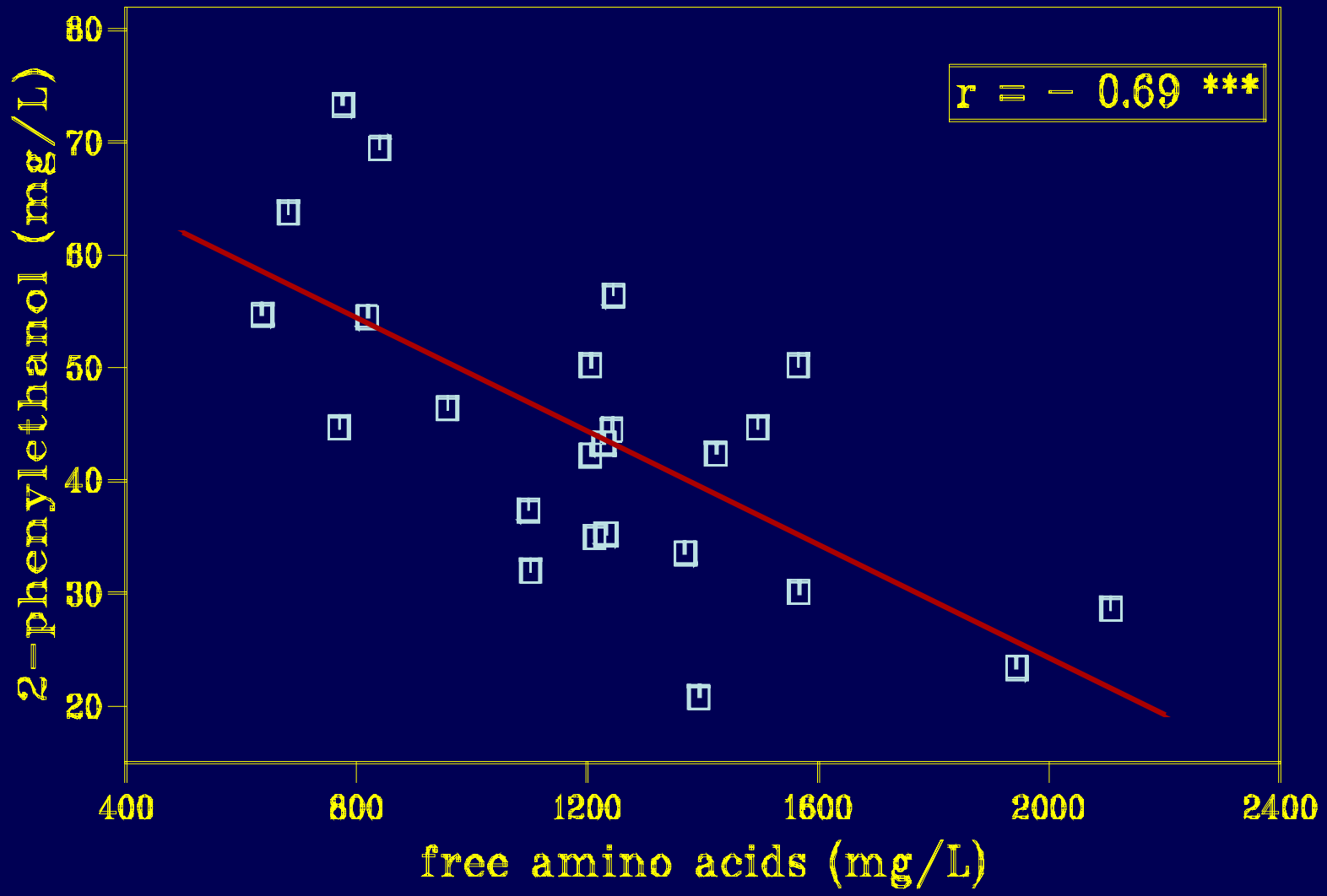
Assimilable nitrogen of 1995 industrial (ind.) and experimental (exp.) Chardonnay and Müller Thurgau musts of Trentino



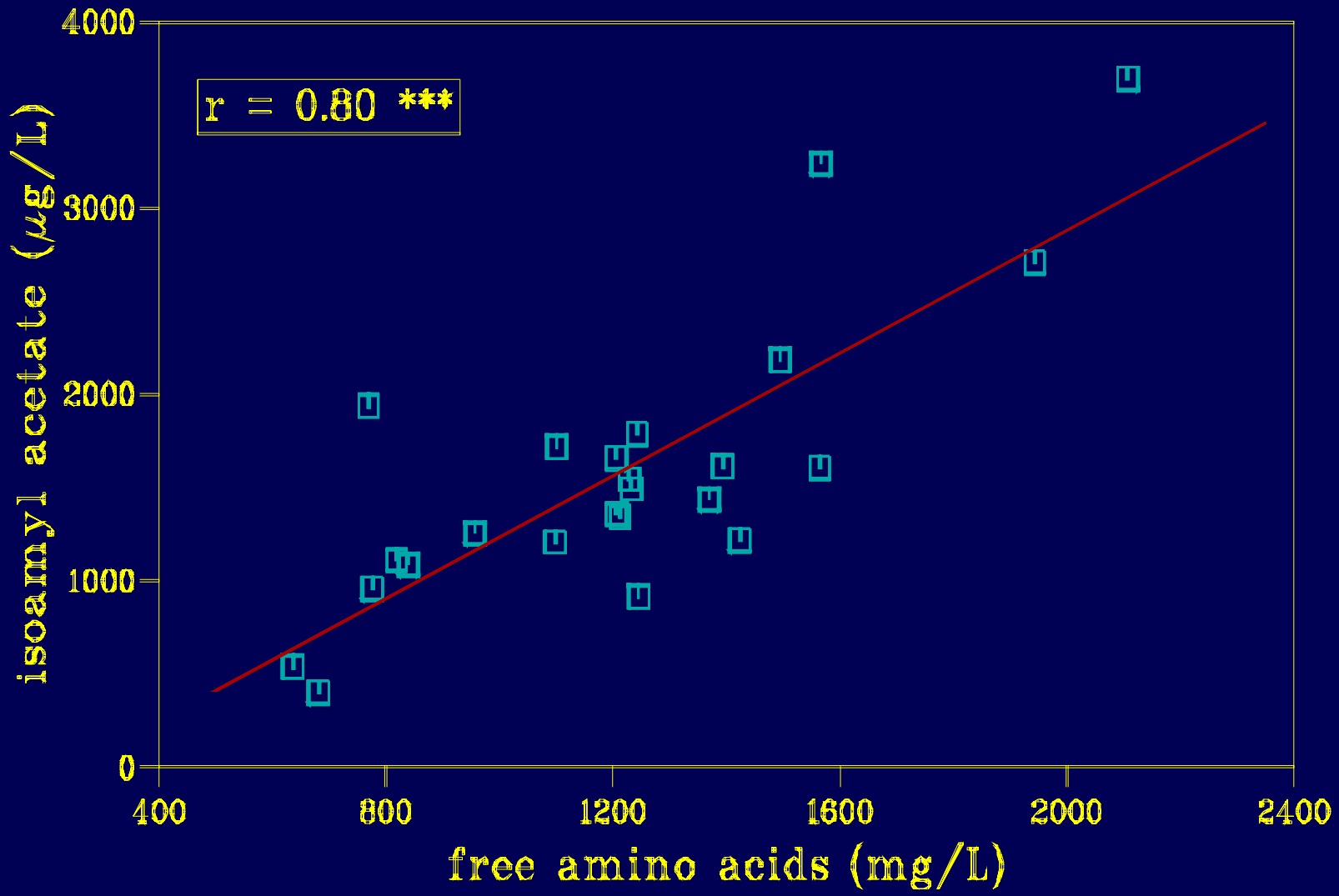


Correlation between free amino acids content in the musts and 2-phenylethanol in the relevant 1993/94 Müller Thurgau (M) and 1986/87/88 Chardonnay (C) wines

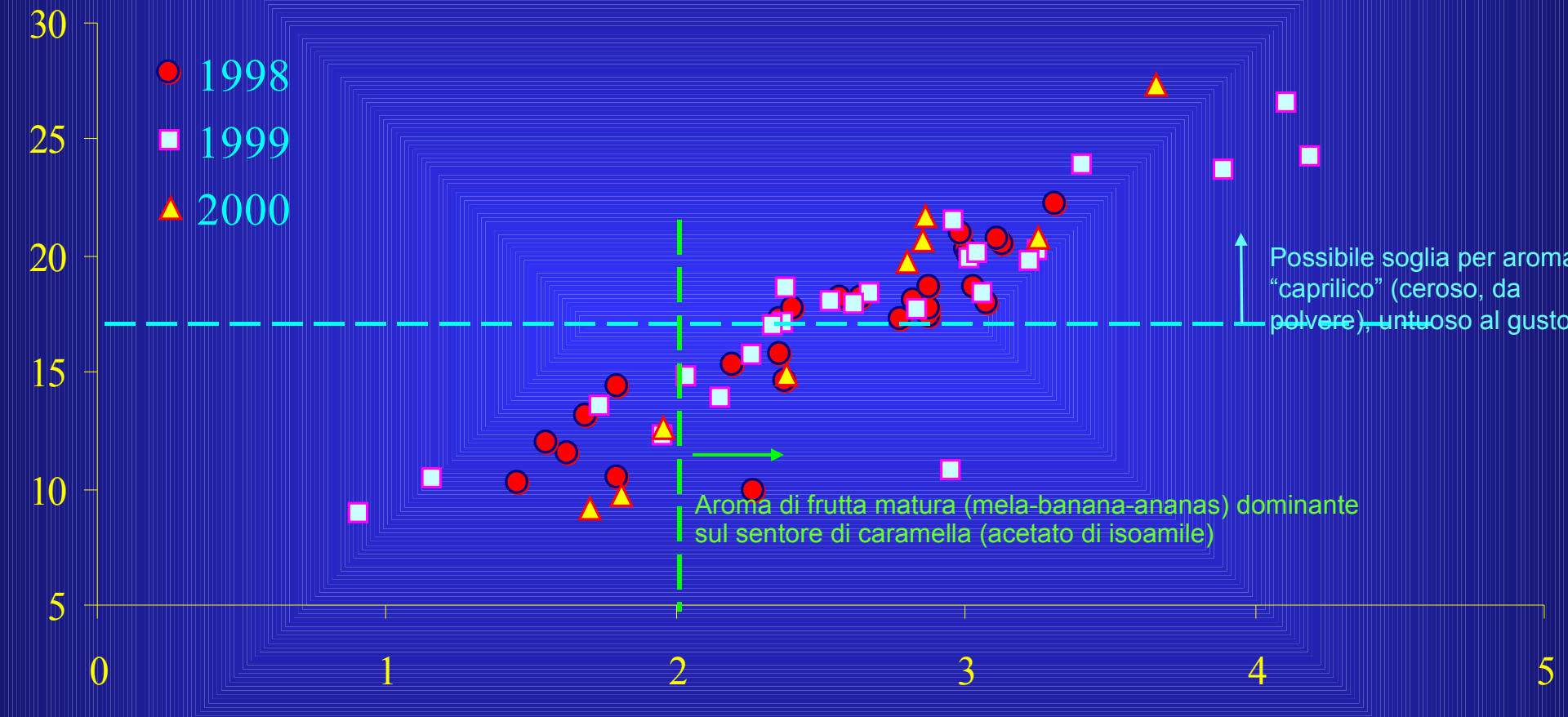
Correlation between free amino acids content in the musts and 2-phenylethanol in the relevant 1993-94 Müller Thurgau wines



Correlation between free amino acids content in the musts and isoamyl acetate in the relevant 1993-94 Müller Thurgau wines

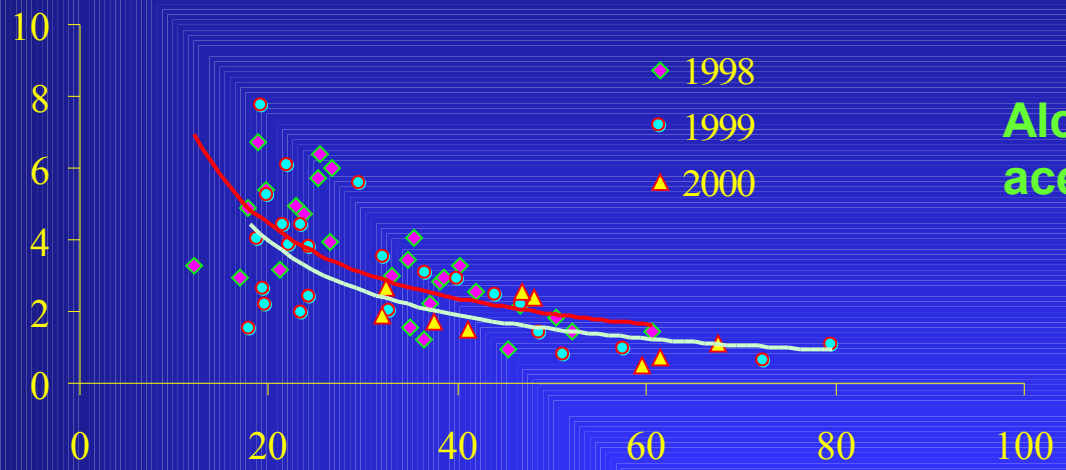


Prosecco: correlazione fra la somma (mg/L) degli acidi capronico, caprilico e caprico (asse Y) e rispettivi esteri etilici (asse X)

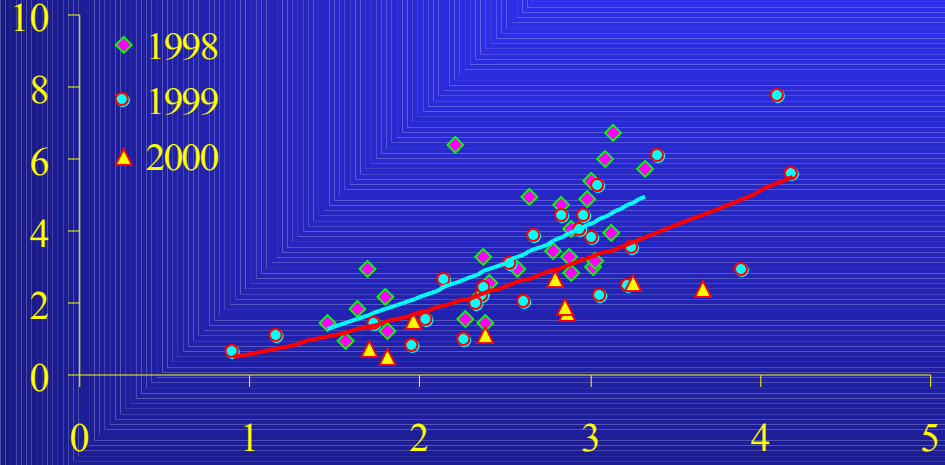


NOTA: correlazione lineare costante tra annate

Prosecco: correlazioni fra composti fermentativi (mg/l) in 3 annate



Alcol β-feniletilico (x)
acetato di isoamile (y)



Σ esteri etilici
(C_6, C_8 e C_{10}) (x)
acetato di isoamile (y)

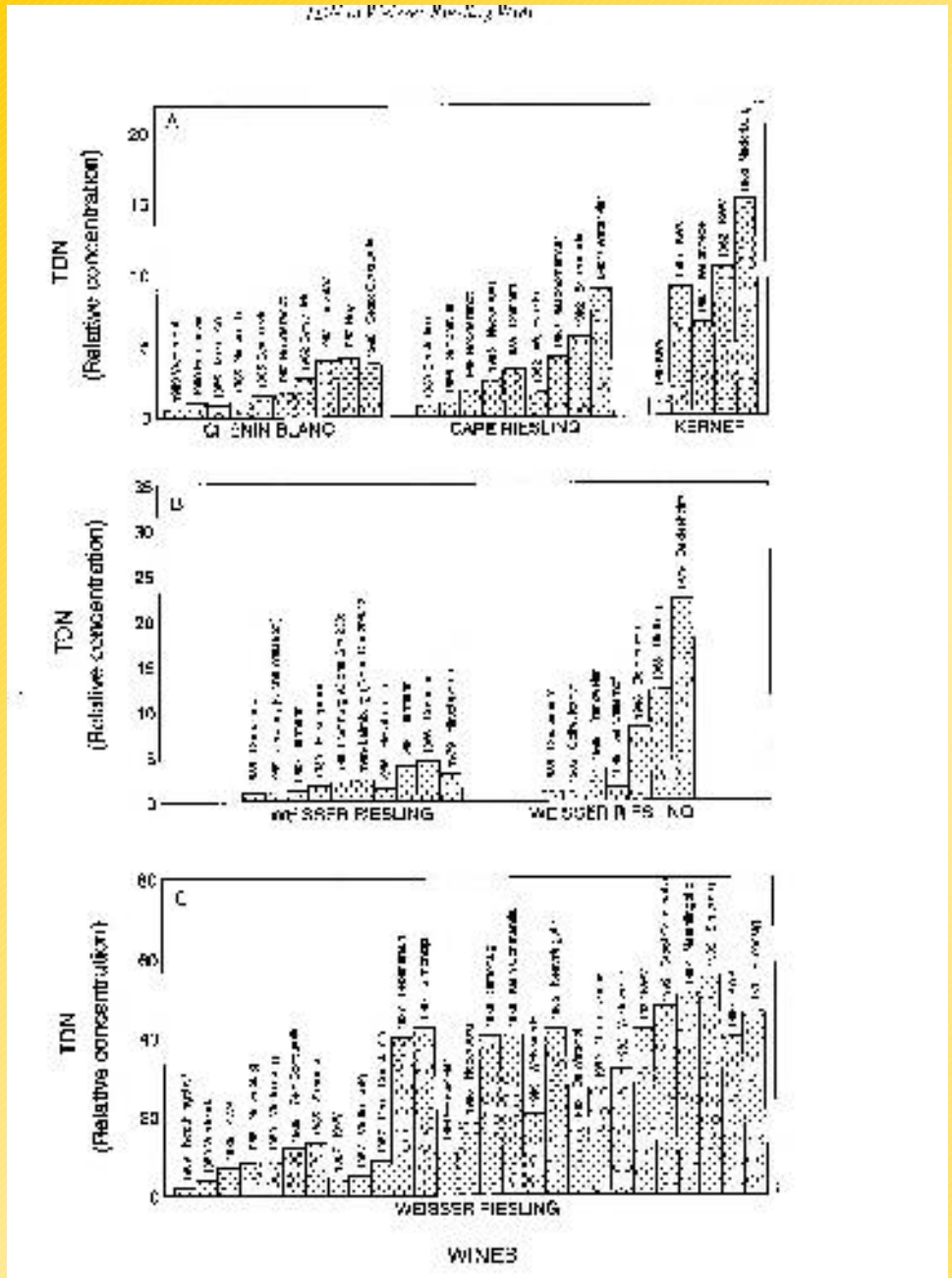
NOTA: costanza negli anni della tipologia di correlazione

Norisoprenoids in Rhine Riesling wines

TDN precursor in Rhine Riesling musts and wines of cool climate growing areas in respect to those of warmer ones:

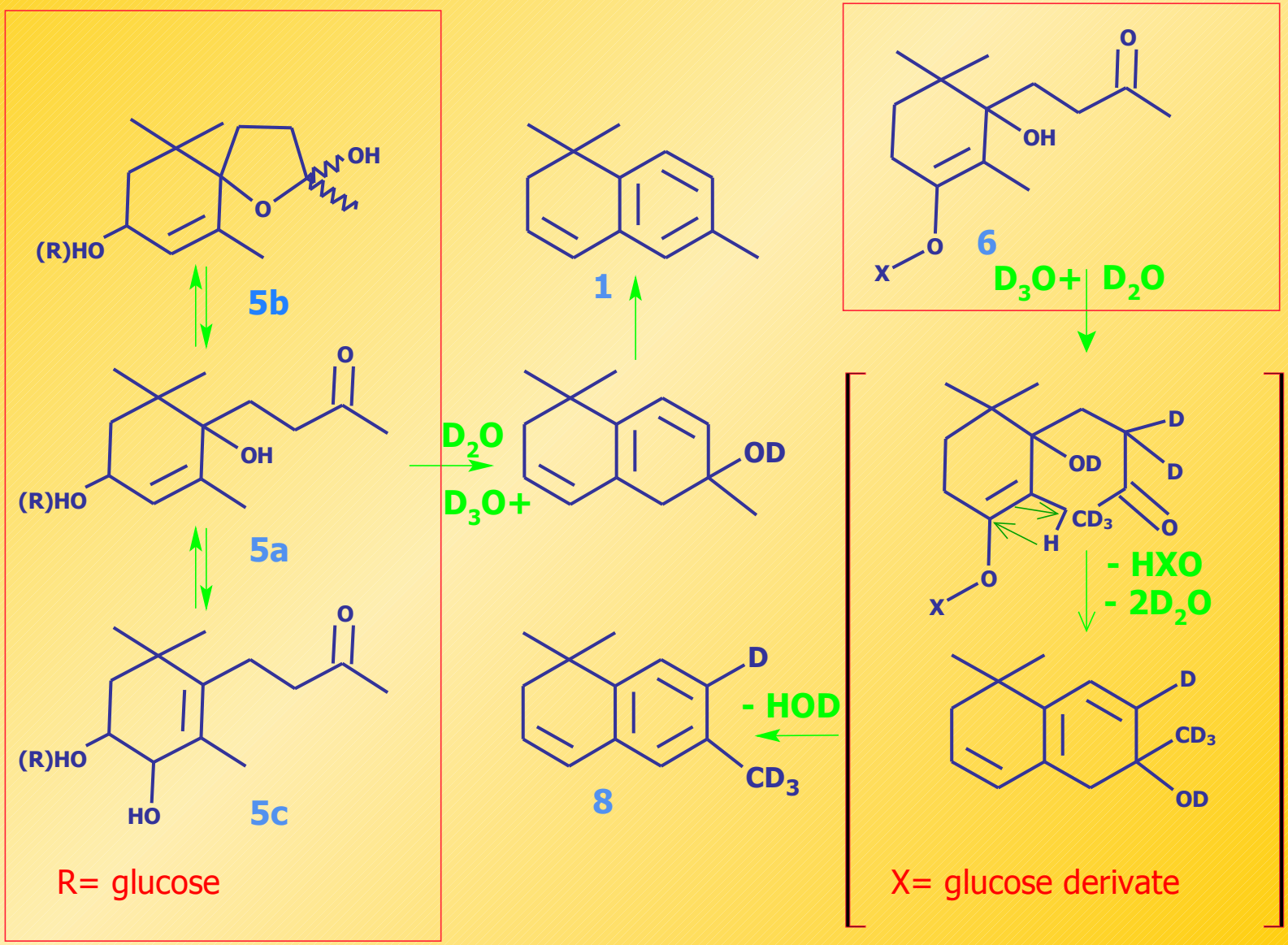
⇨ different dominant possible precursor, but with a formation mechanism mostly kinetically inhibited in wines by normal pH values and storage temperature.
Thus, no remarkable formation of TDN happens in North Italy and in most cooler areas;

⇨ no change of the ratio between the 2 precursors has been ascertained during the grape ripening: thus, the environmental influence works just from the beginning of the biosynthesis.



TDN content of Rhine Riesling and other wine types from different countries (South Africa, Germany and Italy) and vintages/ ageing
(Marais et al., 1992)

Proposed schematic pathway of TDN and TDN-d_4 formation in D_2O substrates (adapted from Winterhalter P., 1991 and Versini et al., 1996)



Chardonnay

Accumulation of TDN, VTP, actinidols, β-damascenone and 3-oxo-α-ionol in Chardonnay grapes by ripening in a hilly area particularly suitable for the production of Reserve sparkling wines.

Norisoprenoids scoring (µg/L) in rather old (6 to 23 years) sparkling wines (pH 2.9-3.1) *(Versini et al., 1996)*

TDN: from 0.8 to 2;

vitispiranes: from 2 to 16;

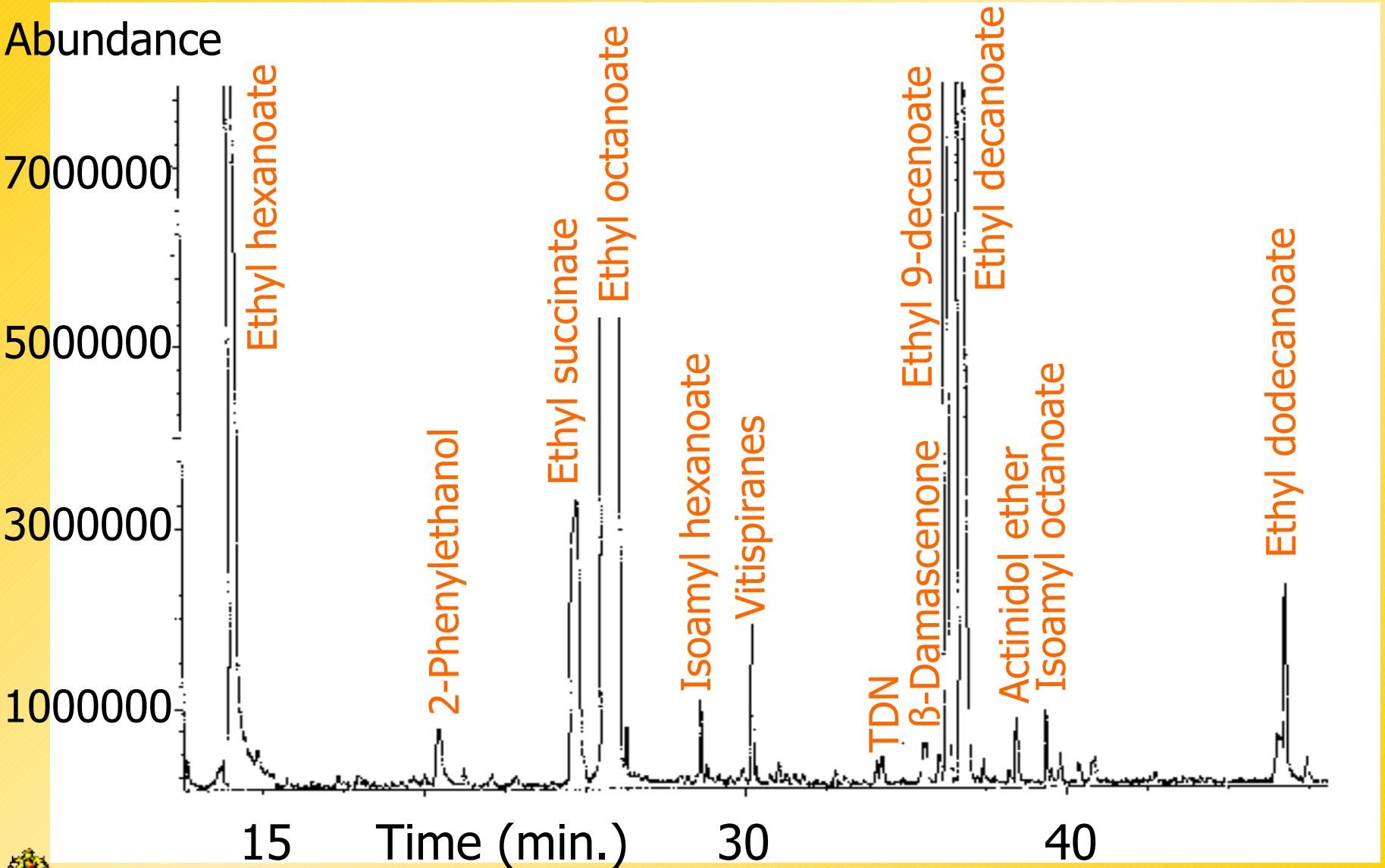
actinidol (1): from 5 to 21;

3-oxo-α-ionol: from 5 to 50

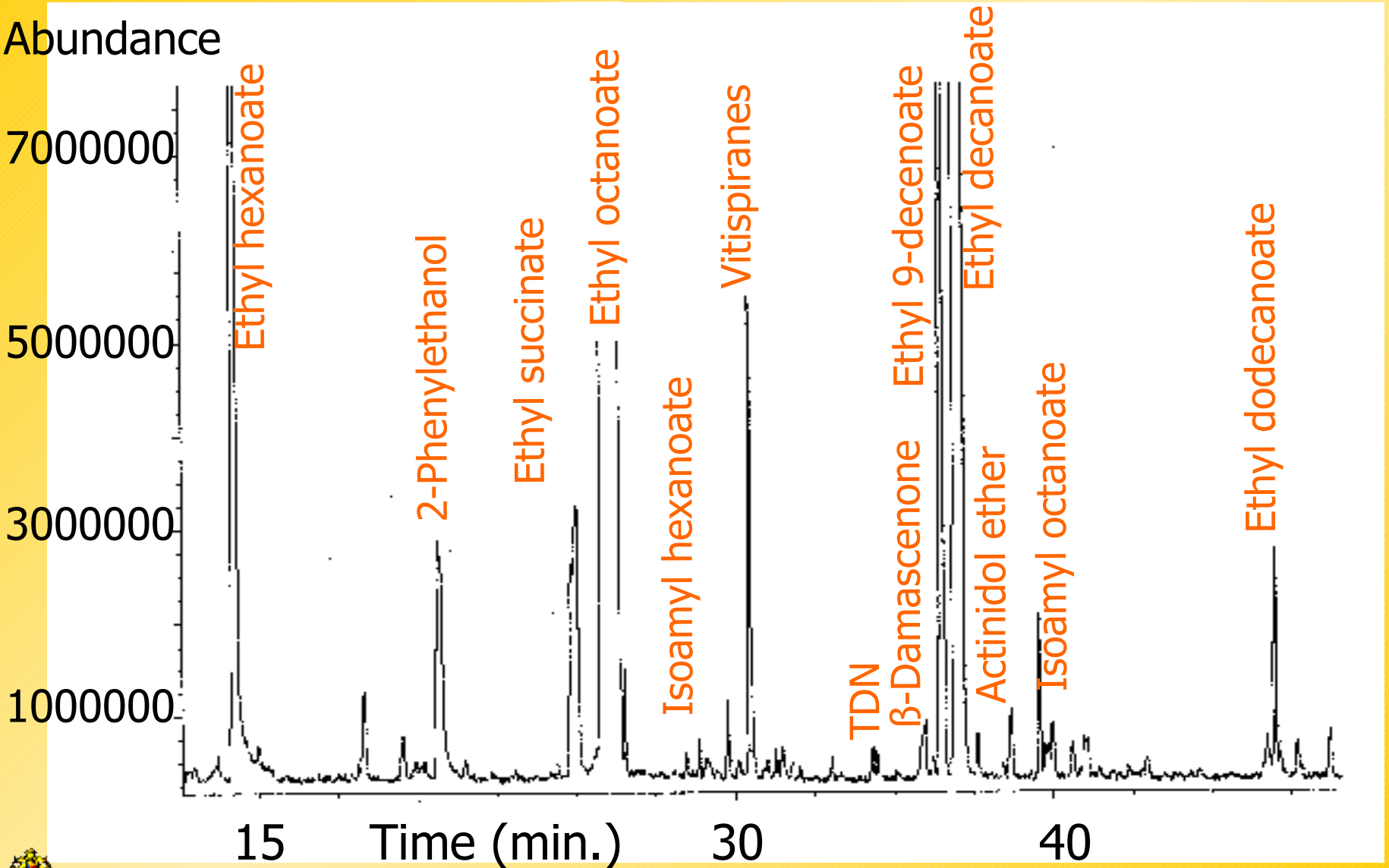
[*residual bound 3-oxo-α-ionol (enzym. free)*: from about 120 to 190]

⇨ Lower values found in younger wines: thus, sensory contributions possible in very old products only.

SPME-GC/MS PROFILE OF A 1983 SPARKLING WINE OF TRENTINO



SPME-GC/MS PROFILE OF A 1964 FRENCH SPARKLING WINE

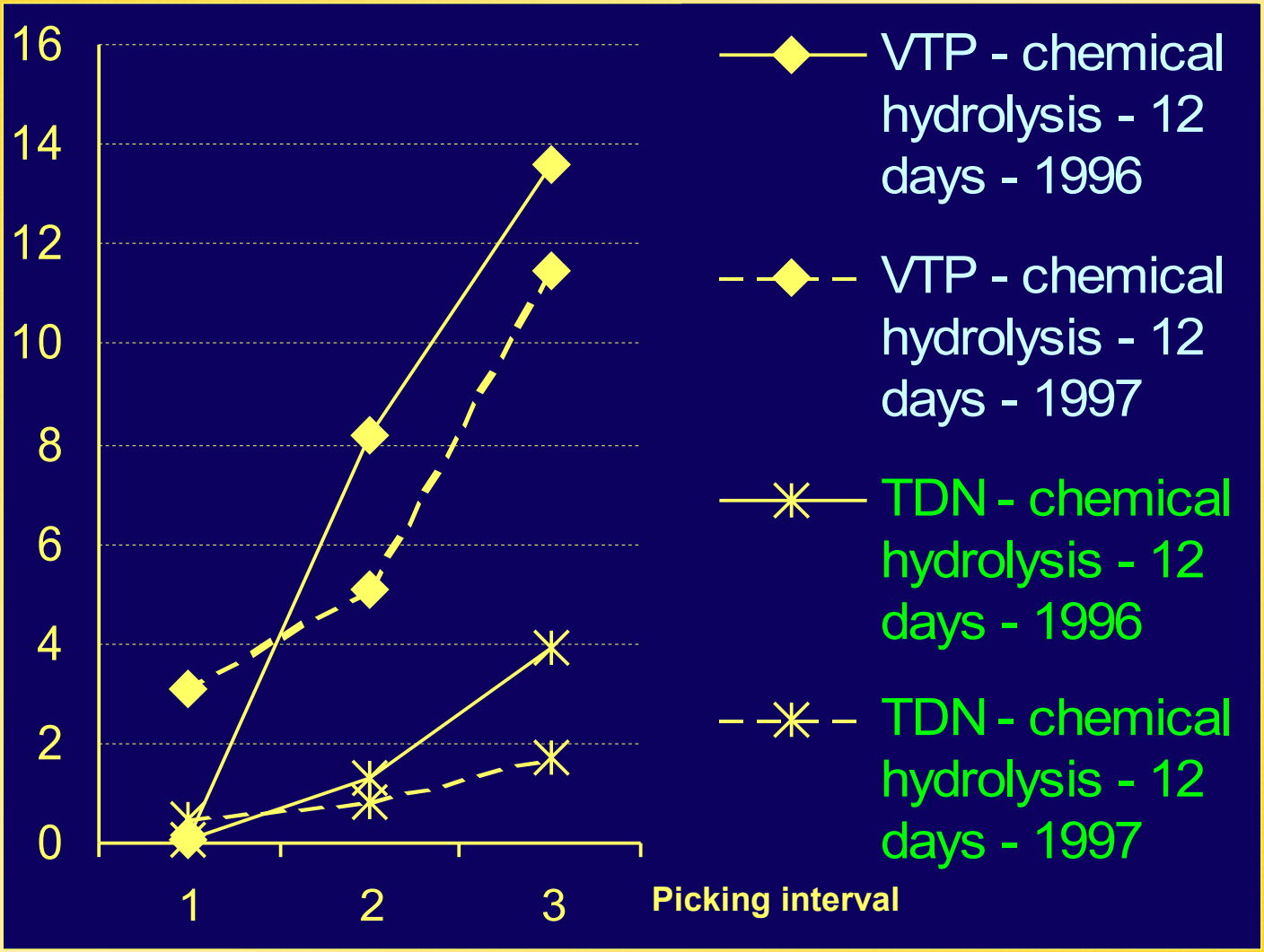


Aglycones after enzymatic (Enz) and chemical (Chem) hydrolysis (pH 2.5, 50°C) of the bound aroma fraction of Chardonnay musts produced on industrial scale

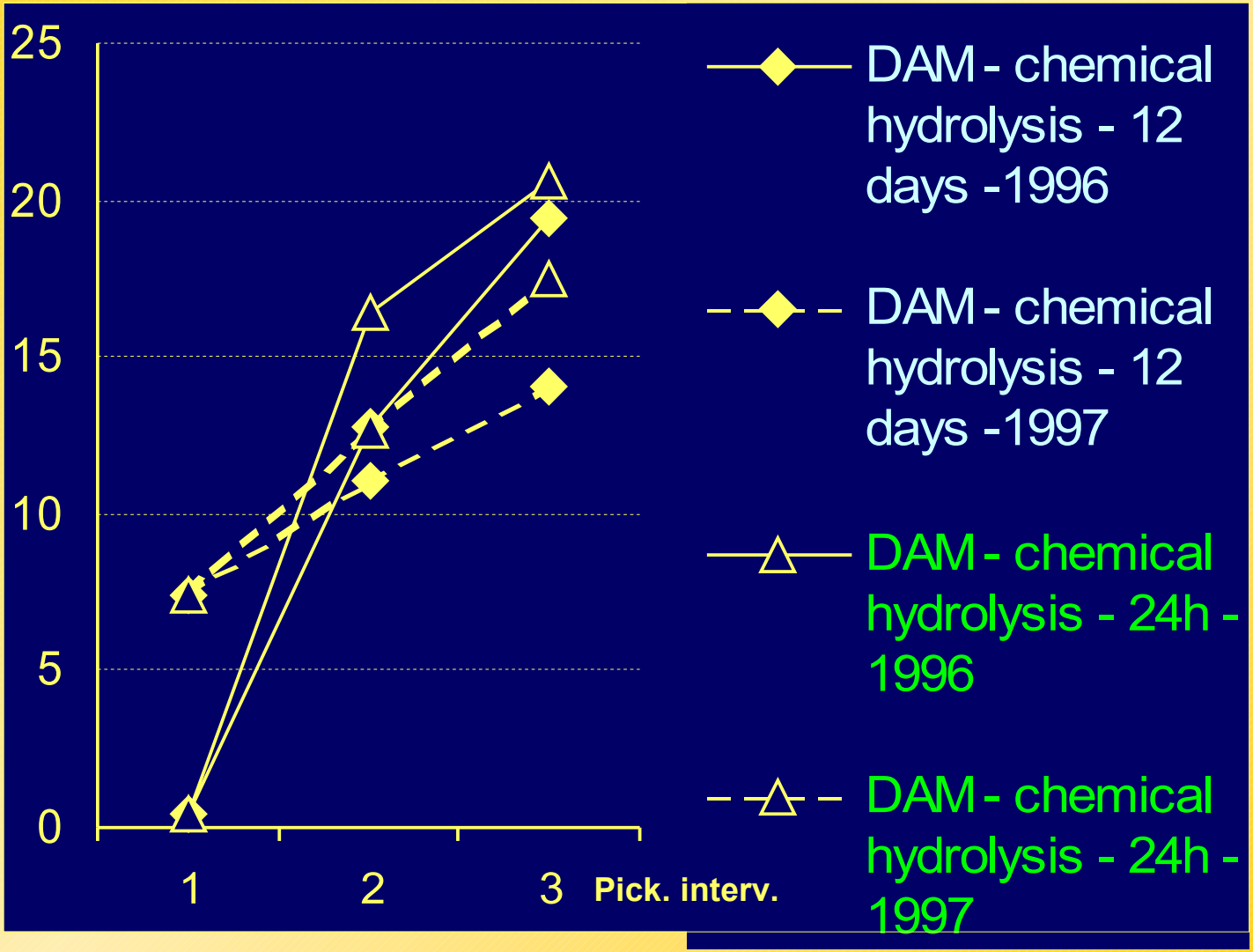
Aglycones (µg/L)	1995				1996			
	Enz		Chem (12 days)		Enz		Chem (12 days)	
	mean (n=7)	*st. dev.*	mean (n=7)	*st. dev.*	mean (n=9)	*st. dev.*	mean (n=9)	*st. dev.*
trans fur. linalool ox.	11.7	*1.5*	54.4	*14.7*	10.4	*4.4*	41.8	*16.0*
cis fur. linalool ox.	1.6	*0.5*	28.7	*7.8*	3.0	*0.7*	22.2	*8.0*
linalool	11.9	*3.6*	2.0 *	*0.6*	11.7	*7.8*	2.6 *	*0.7*
alpha-terpineol	0.4	*0.2*	5.7 *	*1.9*	2.5	*3.2*	5.3 *	*4.2*
ß-damascenone	-	-	15.5	*2.7*	-	-	17.4	*2.5*
trans actinidol (I)	-	-	26.3	*4.1*	-	-	28.8	*9.4*
trans actinidol (II)	-	-	37.6	*6.4*	-	-	41.4	*13.5*
3-oxo-alpha-ionol	173	*37*	12	*2.0*	167	*35.6*	22.0	*8.1*
vitispiranes	-	-	6.0	*2.5*	-	-	10.3	*4.0*
TDN	-	-	2.7	*0.4*	-	-	3.2	*1.7*

* measure after 1 day heating n=samples number µg/L as 2-octanol

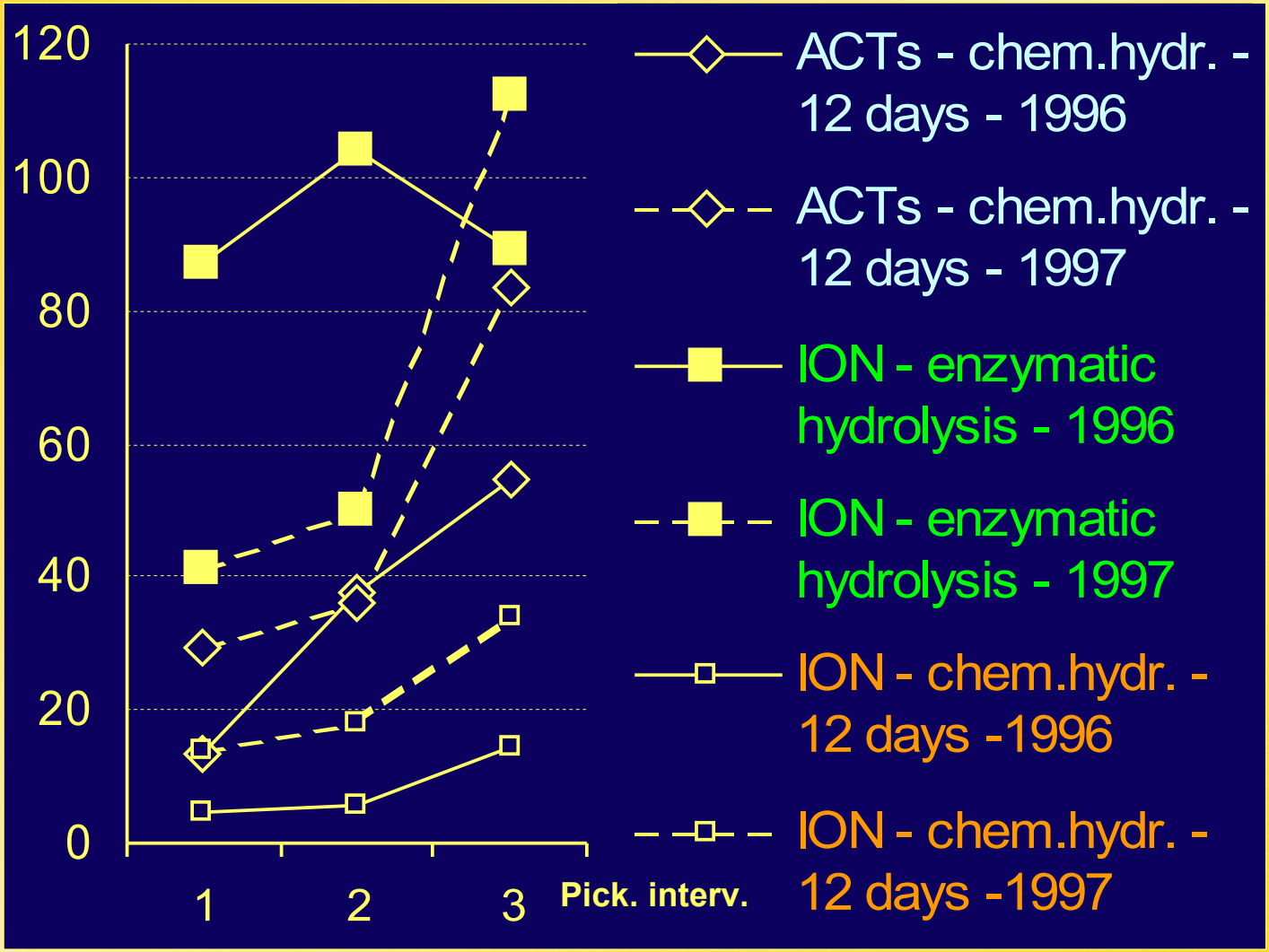
Evolution of some aroma precursors (µg/L) during Chardonnay grape ripening (vineyeard at 650 m asl)



Evolution of some aroma precursors (µg/L) during Chardonnay grape ripening (vineyeard at 650 m asl)

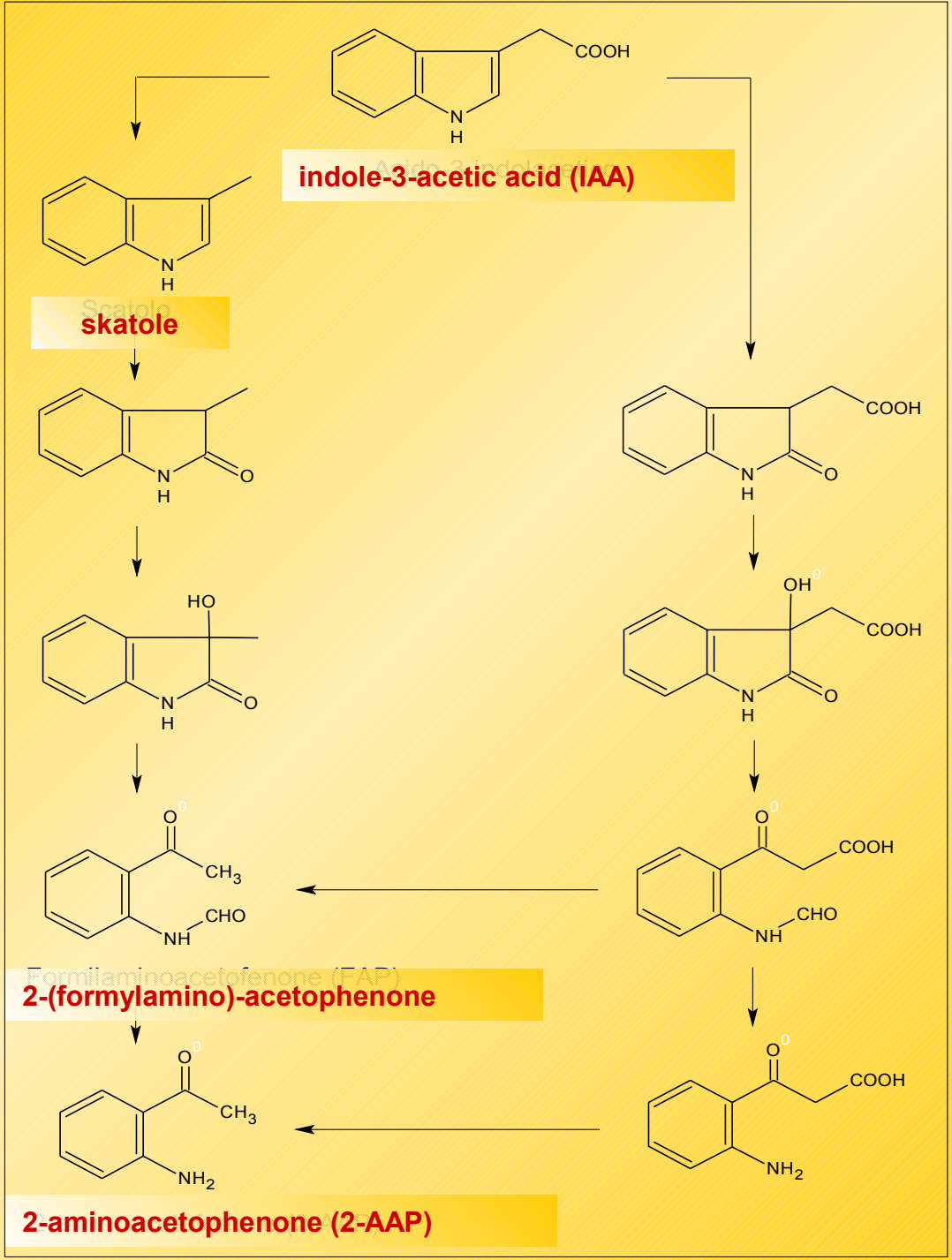


Evolution of some aroma precursors (µg/L) during Chardonnay grape ripening (vineyeard at 650 m asl)



Possible reaction mechanism of IAA to 2-AAP

(Christoph et al., 1998)



Main scents and 2-AAP level of reserve sparkling wines at and some time after the disgorging

PRODUCER/TIPOLOGY	DISGORGING TIME	2-AAP (ug/L)	SENSORIAL NOTES
A 1999 brut: 95% Ch + 5% Pn	26/10/01	<0.05	weak ageing scent, fruity, a little yeasty, no honey-like aroma
A 1999 brut: 95% Ch + 5% Pn	03/02/02	<0.05	weak ageing scent, fruity, a little yeasty, no honey-like aroma
A 1999 brut: 95% Ch + 5% Pn	25/02/02	<0.05	more yeasty than the finished product
A 1993 riserva: 100% Ch	24/09/01	0,35	remark. norisoprenoid-like scent, matured-yeasty, no honey-like aroma
A 1993 riserva: 100% Ch	25/02/02	0,25	more yeasty than the finished product
A 1997 perlé: 100% Ch	05/11/01	<0.05	medium ageing aroma, yeasty, fruity, no honey-like aroma
A 1997 perlé: 100% Ch	25/02/02	0,05	more yeasty than the finished product
B 1997 brut riserva: 100% Ch	autumn 2000	0,41	aged/oxidised, yeasty, resinous, hydrid/honey-like aroma
B 1997 brut riserva: 100% Ch	18/03/02	0,47	stronger yeasty
B brut classico: 100% Ch	autumn 1999	0,57	aged/eucalyptus-lime like, medium hybrid/honey-like aroma
B brut classico: 100% Ch	18/03/02	0,53	in addition, yeasty scent
C 1996 riserva: 70% Ch + 30% Pn	27/06/01	0,20	rather aged, lime/yeasty, weak honey-like scent
C 1996 riserva: 70% Ch + 30% Pn	26/03/02	0,18	in addition, a weak buillon-like scent
C 1988 brut: 80% Ch + 20% Pn	28/06/01	0,22	remark.norisopr./lime-like scent, medium yeasty/aged, no honey-like aroma
C 1988 brut: 80% Ch + 20% Pn	26/03/02	0,29	more yeasty than the finished product
C 1996 brut: 80% Ch + 20% Pn	28/06/01	0,54	weak ageing/eucalyptus like scent, fruity, yeasty, weak honey-like aroma
C 1996 brut: 80% Ch + 20% Pn	26/03/02	0,19	more yeasty than the finished product, no honey/hybrid aroma

Results of comparison of other 'reserve' sparkling wines as for products still on the lees and finished ones *(storage at the same temperature condition for each winery)*

The sensory evaluation realised a possible *honey/hybrid scent* only for some products and usually in correspondence of at least 0.4-0.5 µg/L, close to the threshold level established in still wines. ***No remarkable and off-flavouring levels have been ascertained in this control; on the contrary, a possible positive contribution to the aroma complexity***.

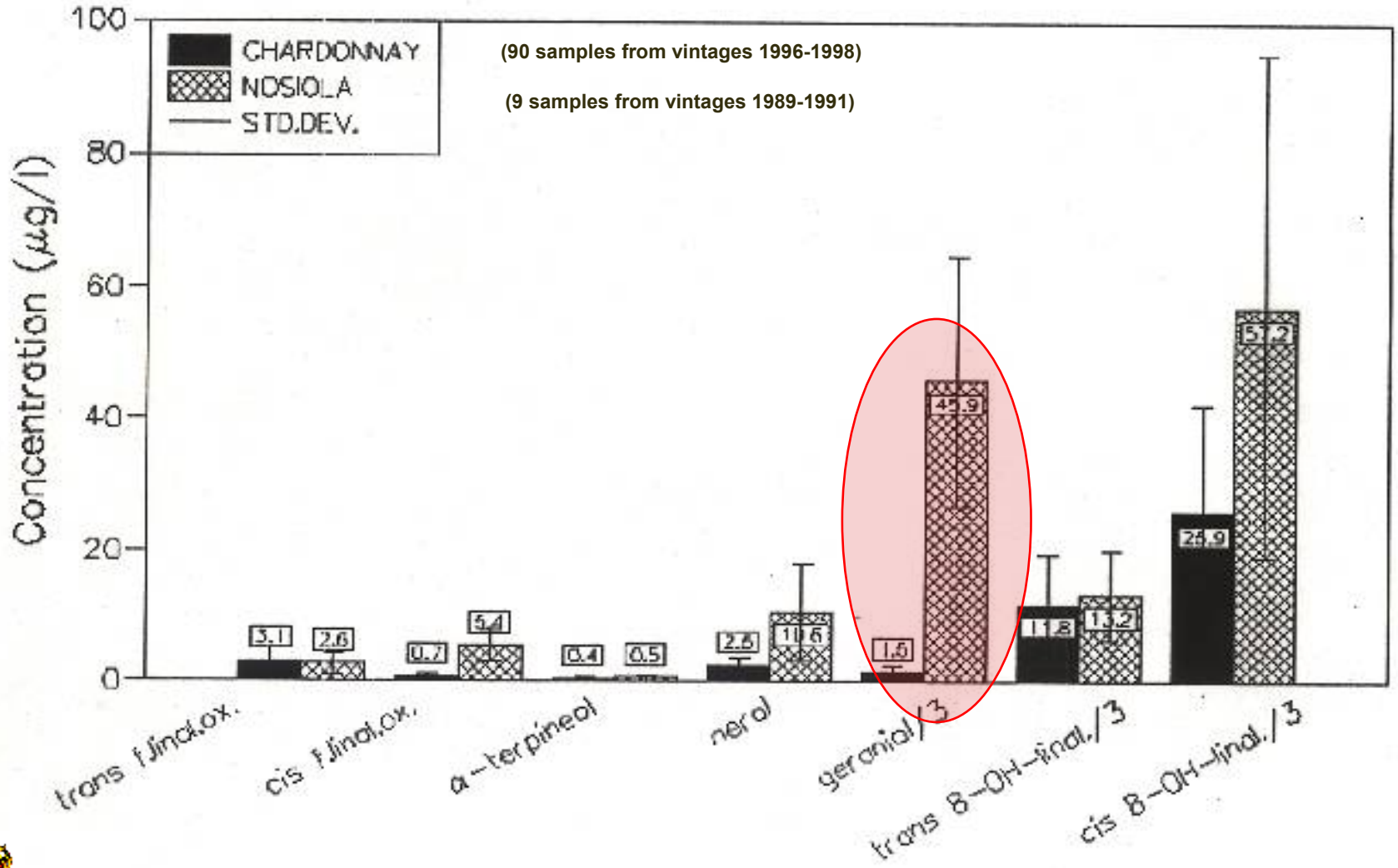
Conclusion:

⇨ no influence of disgorging on the 2-AAP level in finished sparkling wine;

⇨ possible pleasant honey-like scent from 0.3 µg/L of 2-AAP, becoming a still pleasant weakly scenting hybrid-like aroma at about 0.4-0.5 µg/L;

⇨ norisoprenoids-like aroma (aged/eucalyptus-like/resinous scents after 4-5 ageing years.

Examples of discrimination between non-floral varieties: the case of Chardonnay and native Nosiola in the Trentino region - Comparison between the mean content of some bound monoterpenols in musts



Free (f) and bound (b) aroma compounds in juices from different wineries for the production of *Vino Santo*

(Versini et al., 1999)

compounds (µg/L)	winery CS		winery P	
	f	b	f	b
p-cymene	13	nd	<2	nd
limonene	nd	nd	570	nd
linalool	2	23	40	197
tr. fur. linalooloxide	<2	21.5	26	123
cis fur. linalooloxide	<2	18.5	6	16
alfa-terpineol	<2	4	27	8
terpinen-4-ol	77	7	119	5
ho-trienol	4	2	7	3
tr. pyran linalooloxide	<2	7.5	26	40
cis pyran linalooloxide	<2	4	2	8
nerol	<2	95	<2	69
geraniol	2	921	<2	273
ho-diendiol I	43	23	506	135
ho-diendiol II	6	3	38	16
tr. 8-OH-linalool	2.5	165	10	429
cis 8-OH-linalool	4	427	40	845
7-OH-dihydrogeraniol	<2	139	27	32
benzyl alcohol	11.3	1215	5	1792
2-phenylethanol	294	713	3180*	710
1-octen-3-ol	8	nd	45	~2
benzaldehyde	42	nd	55.4	nd

*: partially due to a fermentation onset

compounds	peak n°	1988*	1990°	1992°	1993**	1994°	1995°	1996°	1997°	'88/'90/'92***
monoterpene hydrocarbons										
p-cymene	5	7	13	19	18	21	9	15	<3	nd
limonene	7	6	120	105	174	26	20	7	<3	nd
gamma-terpinene	8	12	21	16	21	24	10	14	<3	nd
alfa-terpinolene	9	5	21	16	14	41	10	17	<3	nd
a p-menthatriene	11	<2	25	8	6	43	12	27	<3	nd
total		*30*	*200*	*164*	*233*	*155*	*61*	*80*	*<10*	*nd*
monoterpenols										
linalool	10	23	108	67	42	144	66	62	16	3
terpinen-4-ol	14	25	18	21	61	67	65	77	25	nd
monoterpenol ethyl ethers										
linalyl ether	13	10	95	43	84	190	25	30	<3	<3
neryl ether	18	8	25	24	28	36	12	7	<3	<3
geranyl ether	21	23	96	58	55	172	40	26	<3	5
alfa-terpenyl ether	16	34	108	93	70	173	52	28	<3	11
a 8-ethoxy-p-menthadiene	19	7	39	15	14	94	46	63	<3	nd
total		*75*	*324*	*218*	*237*	*571*	*129*	*91*	*~10*	~16
other monoterpene derivatives										
anhyd.pyr.linalooloxide	3	6	10	16	14	9	10	12	<3	19
neroloxide	12	9	24	16	18	27	7	14	<3	20
a p-menthadienol acetate	22	8	38	1425	14	63	29	45	9	nd
norisoprenoids										
beta-damascenone (m/z=69)	24	2.5	8.6	8.1	7	11	8.3	10.4	6.1	9
vitispiranes	20	205	189	290	303	146	80	86	6	197
vitispirane ethyl ether (?)	27	20	21	26	31	13	9	13	<3	8
TDN	23	59	50	55	73	40	13	10	<3	151
TDN ethyl ether (?)	28	9	15	11	12	8	3	4	<3	14
actinidol 1	25	18	11	20	23	23	9	4	<3	16
actinidol 2	26	9	6	9	11	12	4	2	<3	7
other compounds										
ethyl cinnamate	28	4	17	13	7	10	8	19	4	nd
ethyl benzoate	12a	6	15	15	6	20	16	24	<3	nd
styrene	2	5	8	13	<3	16	13	46	6	nd
1-octen-3-ol	4	7	6	7	6	14	13	19	4	nd

(°, *, **: different wineries; ***: mean values of three wines from grapes vinified at the harvesting)

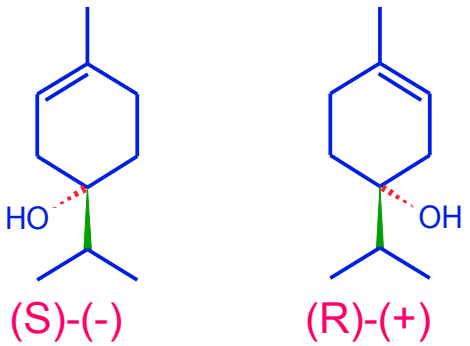
Aroma compounds in the headspace of *Vino Santo* from different vintages quantified using SPME technique (relative values to internal standard)

Free and bound monoterpenols of Vino Santo from different vintages quantified after adsorption on XAD-2 resin (µg/L as 1-heptanol)

compounds	1988*	1990°	1992°	1993**	1994°	1995°	1996°	1997°	'88/'90/ '92***
free forms									
cis fur. linalooloxide	9	51	28	28	18	15	82	44	11
tr. pyr. linalooloxide	4	54	42	29	72	30	48	20	11
linalool	24	101	81	55	183	74	57	16	3
terpinen-4-ol	71	64	62	187	184	186	230	107	nd
ho-trienol	23	47	49	60	65	50	16	15	8
alfa-terpineol	31	104	67	80	157	65	53	11	17
geraniol	15	50	29	10	47	39	93	30	<5
ho-diendiol I	54	451	323	260	962	305	231	41	61
ho-diendiol II	6	25	25	21	85	20	15	4	4
bound forms as aglycones									
tr. fur. linalooloxide	33	171	83	123	242	109	89	61	48
cis fur. linalooloxide	42	50	46	52	68	40	28	27	39
tr. pyran linalooloxide	8	67	26	42	93	30	22	16	11
cis pyran linalooloxide	12	24	14	18	30	21	14	8	16
linalool	nd	14	3	3	59	12	6	4	<1
terpinen-4-ol	<1	2.5	<1	4.5	5	9	11	2.3	<1
alfa-terpineol	5	16	5	26	40	21	9.5	21	6
nerol	25	36	26	32	85	37	22	43	2.5
geraniol	146	110	110	96	304	130	39	236	8.5
ho-diendiol I	9	97	47	77	149	77	36	26	16.5
ho-diendiol II	<2	44	5	15	53	11	2	3	<2
tr. 8-OH-linalool	50	301	103	195	368	207	125	101	15.3
cis 8-OH-linalool	224	272	179	237	265	305	264	190	20.3
7-OH-dihydrogeraniol	76	99	59	189	88	98	28	105	40.7

(°, *, **, ***: see Tab.2)

4-terpinenol



Odour: spicy, nutmeg like, woody-earthy, and also lilac like

Threshold level in wine: about 100 μg/L

Scent of the enatiomeric forms:

(S)-(-)-4-terpinenol: musty, dusty

(R)-(+)-4-terpinenol: musty

Presence of terpinen-4-ol in grapes and/or wines according to the literature

- trace compound in some *Vitis vinifera* (Schreier *et al*., 1976) and some hybrids of *Vitis labrusca* (Stern *et al*., 1967; Schreier *et al*., 1981) products, probably from chemical transformations of monoterpenes;
- basic contributor to the peculiar aroma of the native Japanese variety Koshu (Shimizu and Watanabe, 1981);
- never found as a metabolite of monoterpenes by *Botrytis cinerea* (Bock *et al*., 1986; Rapp and Mandery, 1987)

Peculiarities of *Vino santo* aroma:

Terpenes

- ✓ remarkable presence of terpinen-4-ol and of several common monoterpenols, enhancing floral scents;
- ✓ interesting presence of monoterpene hydrocarbons in the wine head-space;
- ✓ differences among wineries, possibly due in some cases by a little contribution of muscat grape: see also the different aroma profile of two musts, both - however - containing noticeable terpinen-4-ol;
- ✓ aglycones profile rather similar among the products and mostly corresponding to that of normal wines;
- ✓ a rather stable presence of both free and bound forms even in older wines: possible important role of the quite high pH at about 3.8;

Soave DOC wine:

⇨ according to the Appellation rules (DPR 18/6/92 modifying DPRs 06/05/76 and 21-22/10/68), the wine is obtained either only from Garganega grapes or from 70% Garganega plus 30% of Trebbiano di Soave/Chardonnay/Pinor blanc;

⇨ ***aroma description***: fruity with a peculiar 'white blossoms' scent. *Other descriptors*: from green apple-like to banana/ripened fruits-like; violet/acacia blossom-like, honey-like/spicy, almond/cinnamon-like scents.

Free and bound aroma compounds in 2001 and 2002 Garganega and Trebbiano di Soave wines

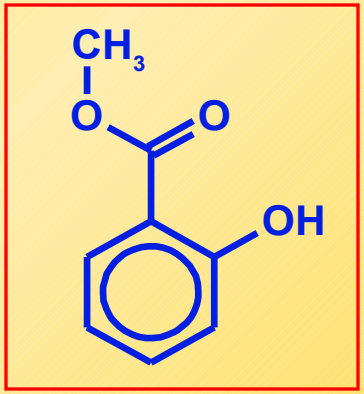
	Garganega (3) 2001 C.Soave+Az.Gini	Garganega (3) 2002 C.Soave+Az.Gini	Trebbiano di Soave (2) 2002 C.Rizzotto	Trebbiano di Soave (2) 2002 C.Soave
Free forms				
linalool+α – terp+geraniol	11.6	9.7	12.4	5.0
ho-diendiol (I)	***26***	***80***	***16***	***25***
methyl salicylate	***7.0***	***3.0***	***45.0***	***33.5***
Bound forms				
benzyl alcohol	***1224***	***1203***	***2877***	***1825***
trans furan linalool oxide	6.9	13.1	14.2	7.1
cis furan linalool oxide	3.7	2.6	19.6	14.2
R(trans/cis)	***1.8***	***5.1***	***0.7***	***0.5***
α -terpineol	***<0.5***	***0.5***	***14.3***	***11.1***
nerol+geraniol	*13.4*	*19.7*	*14.6*	*8.2*
trans 8-hydroxylinalool	19	22	33	17
cis 8-hydroxylinalool	31	129	30	16
R(cis/trans)	*1.7*	*5.9*	*0.9*	*1.0*
methyl salicylate	***99***	***76***	***935***	***459***

Garganega and Trebbiano di Soave wines:
typical primary/prefermentation derived free and bound compounds

Peculiarities:

⇨ possible aroma-influencing presence of ho-diendiol (I) mostly in Garganega wines;
⇨ original presence of methyl salicylate as free and bound form in Trebbiano di Soave wines (about 1/10 in Garganega wines!);
⇨ remarkable presence of benzylic alcohol as bound form in Trebbiano di Soave;
⇨ bound α-terpineol and relevant hydroxylated forms only in Trebbiano di Soave;
⇨ different ratios between some bound monoterpenols useful to check variety.

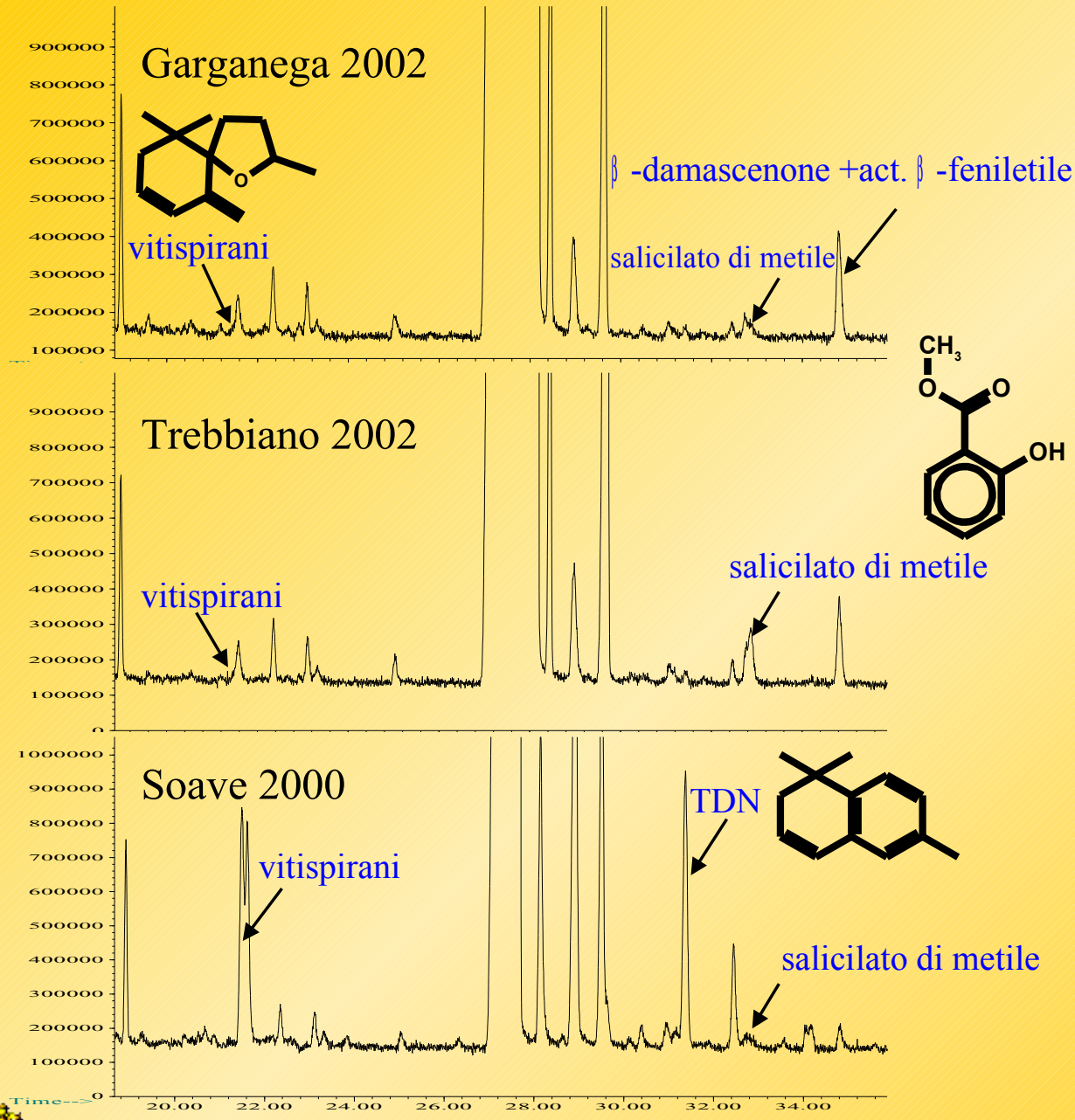
Methyl salicylate a typical wintergreen oil balsamic scenting compound (Bauer & Garbe, 1985)



Sensory tests (duo-trio test with 7 tasters) by adding methyl salicylate to neutral and not remarkably fruity wines as those quoted, proved:

- a threshold level of difference of about 50 ug/L *(chestnut/meadow honey-like scent, partially masking others especially fruity smell),* i.e. at the level found in the Trebbiano di Soave wines and close to the threshold in water of 40 ug/L (Buttery et al., 1971).
- impact threshold close to **100 ug/L.**

According to Meilgaard's theory of the sensory contribution of a substance in a matrix at one fifth of its difference threshold value, a possible aroma involvement of methyl salicylate in Garganega wines aroma could not be ruled out.



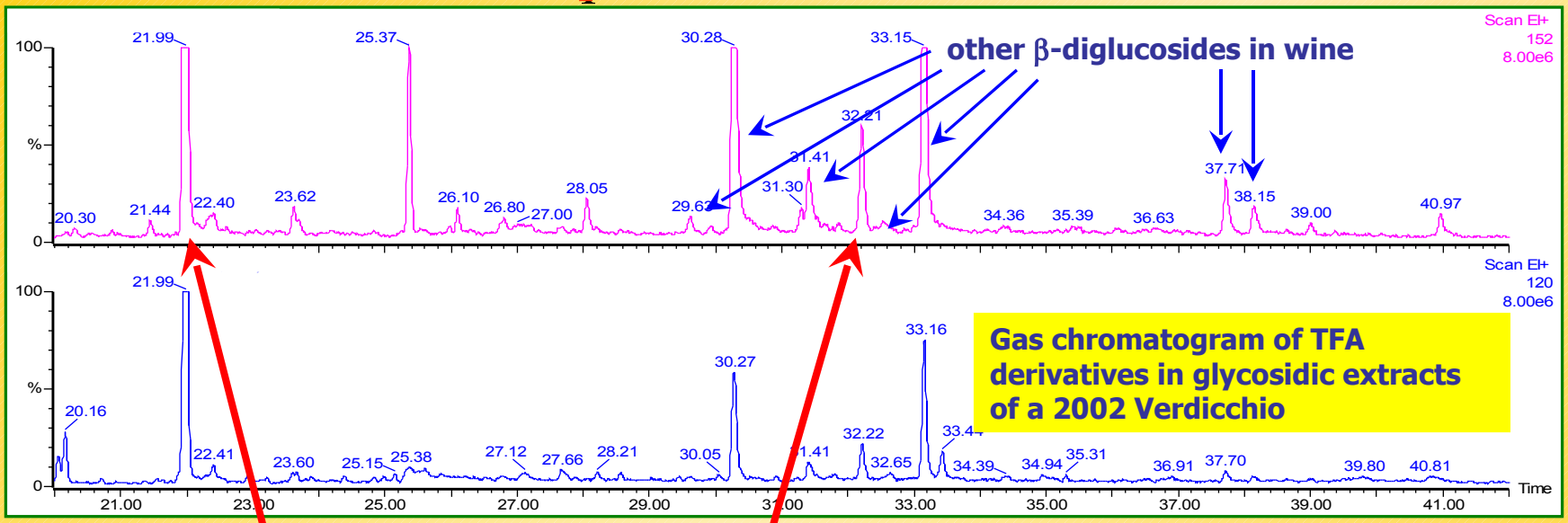
HS-SPME/GC-MS profile in some monovarietal and Soave DOC wines: *variety and ageing effect*

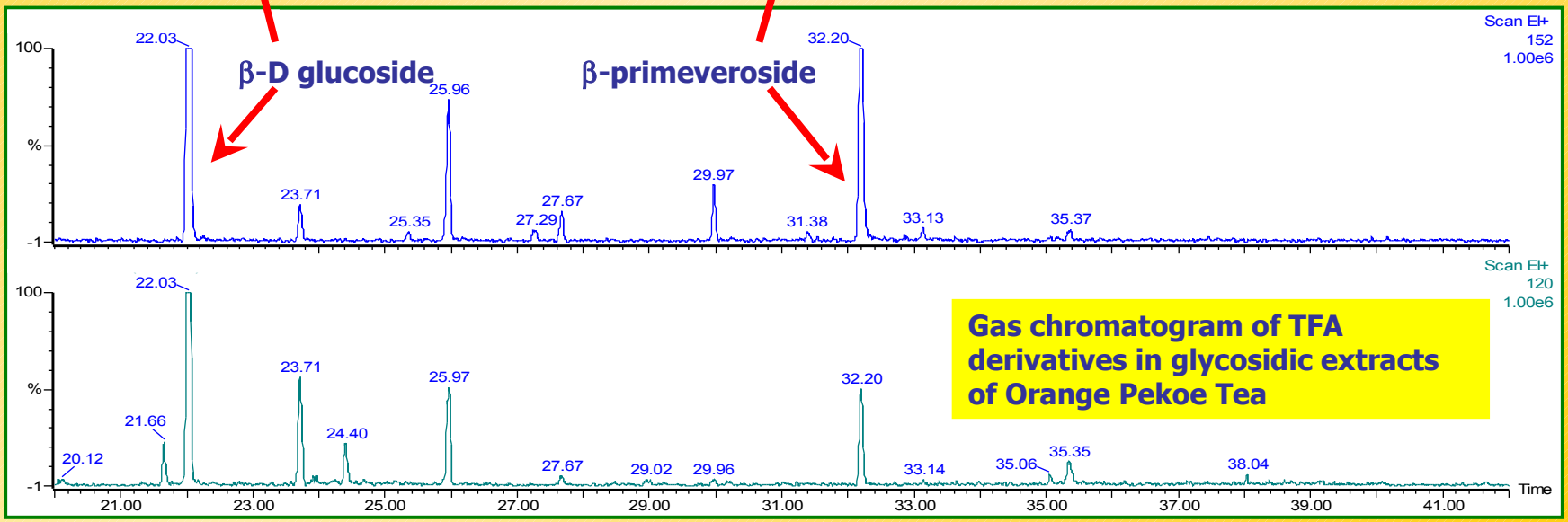
Comparision between 2002 Trebbiano di Soave and Verdicchio wines as for free and boud compounds

Identical profiles according to ampelographic and genetical investigation
(Calò et al., 1991; Grando, unpublisced results)

	VERDICCHIO dei Castelli di Iesi	TREBBIANO di SOAVE C. Soave
free compounds		
3-met.butanol/2-met.butanol	7.0	5.7
linalool	3.3	1.0
α - terpineol	7.7	1.6
geraniol	9.8	0.6
ho-diol (I)	17	10
benzyl alcohol	274	413
2-phenylethanol	23563	19875
1-hexanol	2096	1606
trans 3-hexen-1-ol	67	30
cis 3-hexen-1-ol	79	104
cis 2-hexen-1-ol	20	8
methyl salicylate	10	32
bound compounds		
trans furan linalool oxide	9.4	9.0
cis furan linalool oxide	17	15
trans pyran linalool oxide	6.6	4.0
cis pyran linalool oxide	3.0	2.8
linalool	1.9	0.2
α - terpineol	10	11
nerol	4.1	3.9
geraniol	15	5.0
ho-diol (I)	26	6.0
benzyl alcohol	2039	2253
methyl salicylate	453	489

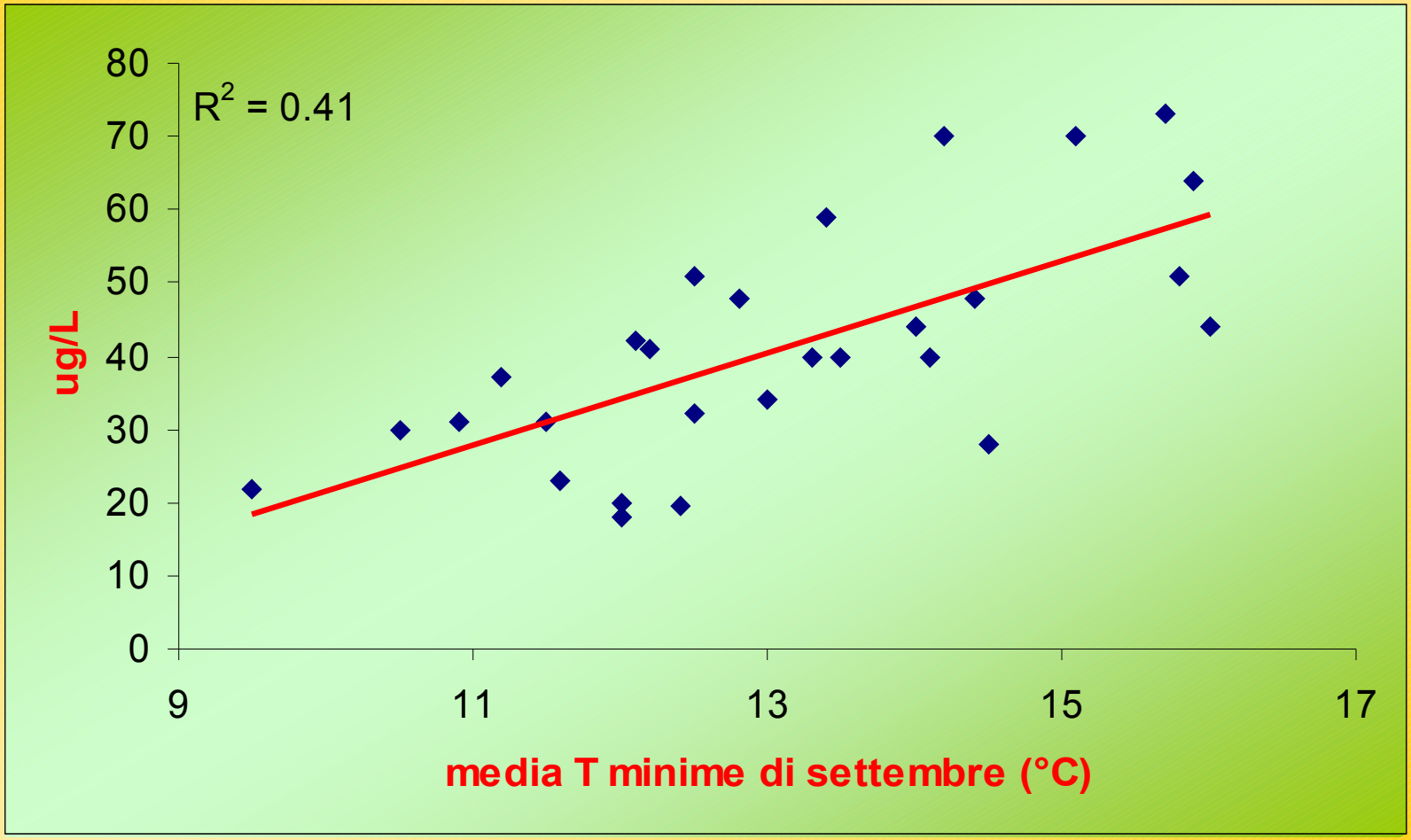
Possible precursor of methyl salicylate: GC-MS profile of TFA derivatives



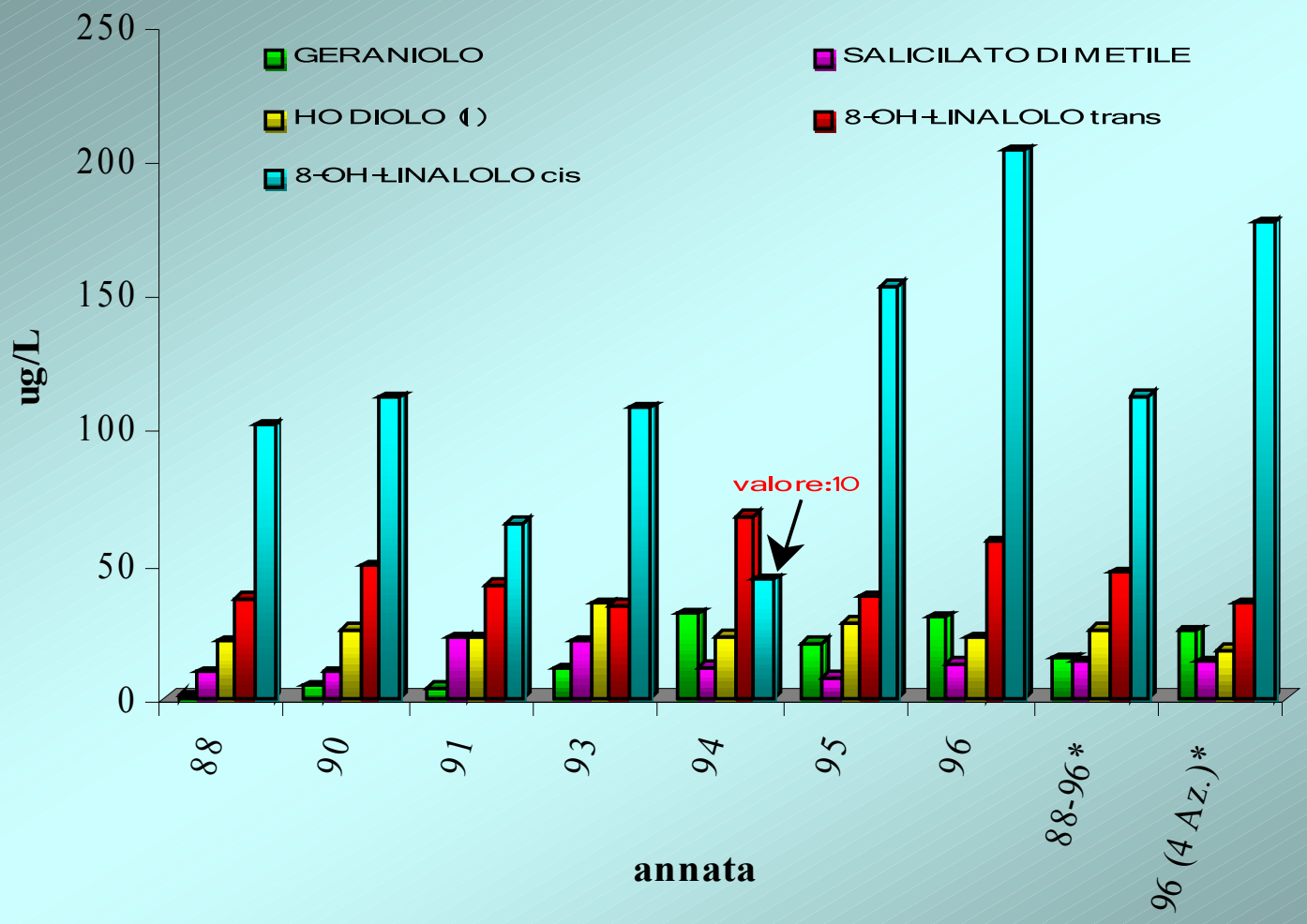


(Versini et al., In Vino Analytica Scientia 2005)

Relazione tra temperature minime di settembre e la presenza di salicilato di metile in forma legata nell'uva di Garganega (In: “Le vigne del Soave”- Di Stefano et al., 2002)



Vini Recioto di Soave DOCG: alcuni composti in forma legata - Az. A: diverse annate; tutte le Az. - annata 1996: valori medi

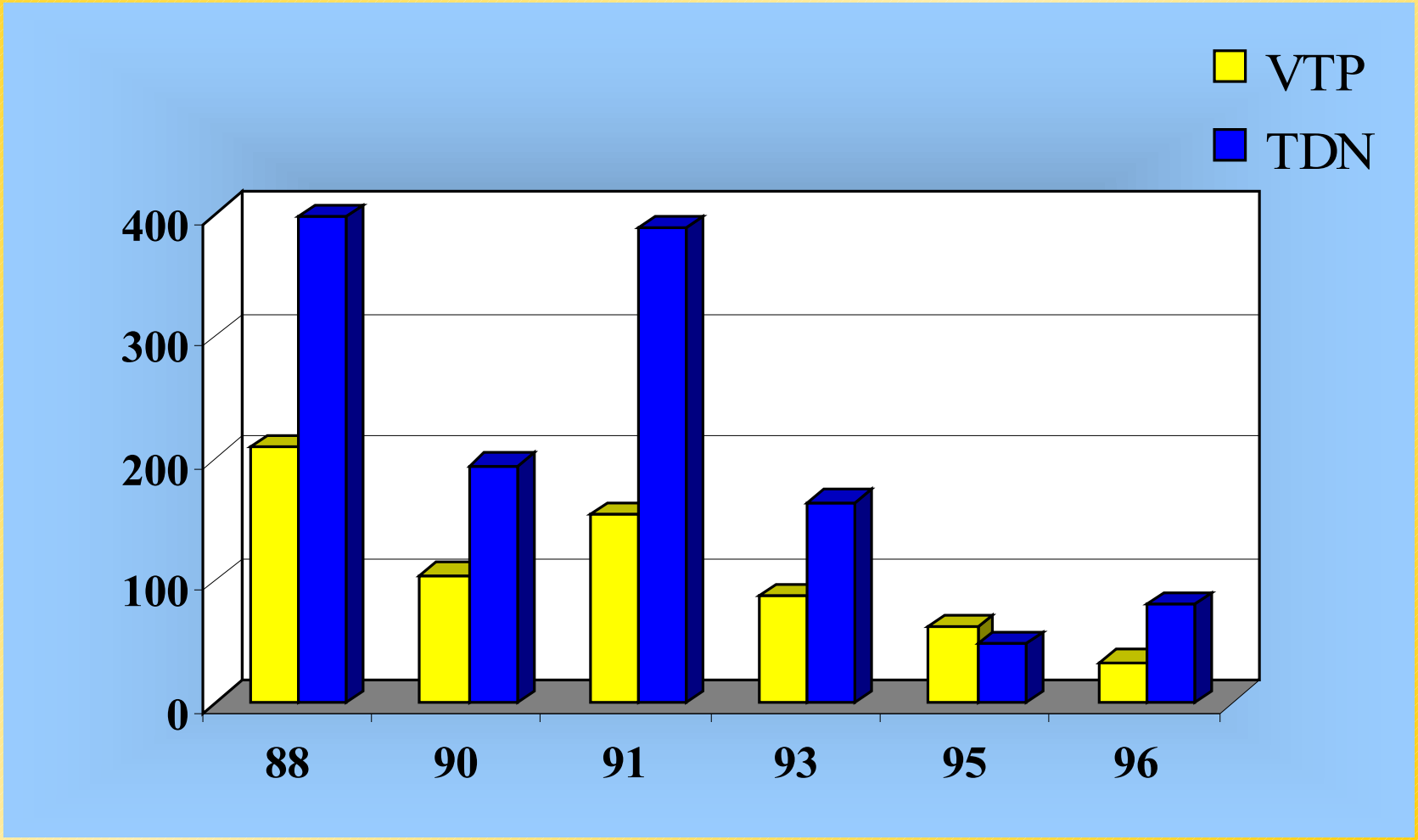


In: “Il Recioto di Soave”, Versini et al., 1998

Basic analyses of "passiti" wines of different wineries and vintage years

	VINO SANTO			AMARONE			RECIOTO		
	mean n=8	max	min	mean n=7	max	min	mean n=7	max	min
Alcohol. proof (% Vol)	10,7	12,3	6,2	14,7	15,0	14,5	12,5	13,4	11,4
Total sugar (g/L)	161,4	273,0	104,0	5,1	8,2	2,8	99,9	131,0	77,1
Tot. alcohol. proof (% Vol)	20,4	22,6	18,6	15,0	15,4	14,7	19,2	19,9	18,1
pH	3,78	3,91	3,65	3,50	3,67	3,40	3,20	3,37	3,06
Tot. acidity (as H_2T, g/L)	7,23	9,40	5,90	5,50	6,40	5,00	5,60	6,10	5,30
Glycerol (g/L)	14,16	18,10	10,42	10,10	10,94	8,49	9,70	10,40	8,80
Gluconic acid (g/L)	2,68	4,98	1,03	1,40	3,09	0,55	0,70	1,40	0,27

Vitispiranes (VTP) and 1,1,6,-trimethyl-1,2,-dihydronaphthalene in the headspace (GC-MS SPME analyses; relative ratios to I.S. [TIC/m/z45]x100) of Recioto wines from same winery and different vintages



Content of some aroma compounds in "passiti" wines from different wineries and vintages (mean, max, min)