

STEBA Workshop, December 4th, 2020

Characterization of Emilia-Romagna wines by high resolution mass spectrometry and nuclear magnetic resonance: case study on commercial Lambrusco and minor variety wines of *Vitis vinifera* L. newly registered in the National Register of Varieties

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Tutor: Prof. Andrea Antonelli

Co-Tutor: Dr. Francesca Masino

Commercial wines

Ancellotta (a.k.a. Rossissimo)

Two vinification processes:

1. Red winemaking
2. White winemaking

Two different agronomic management:

1. Integrated
2. Organic

Two vintages:

1. 2018
2. 2019

Malvasia Aromatica di Candia

Two types:

1. Sweet (5 samples)
2. Dry (10 samples)

From 13 different Emilia-Romagna wineries.



Minor red wines

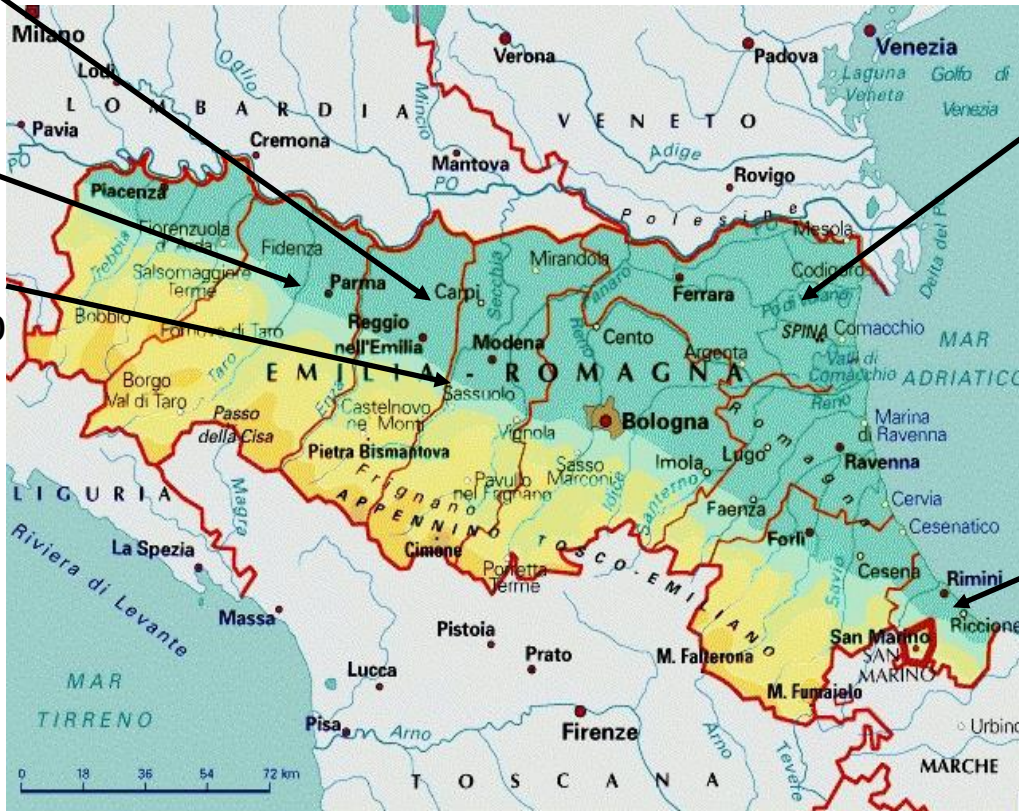
Ancellotta

Termarina
rossa

L. di Fiorano
and Festasio

Rossiola

Veruccese



Minor white wines

Melara and Santa Maria

Malvasia Aromatica di Candia

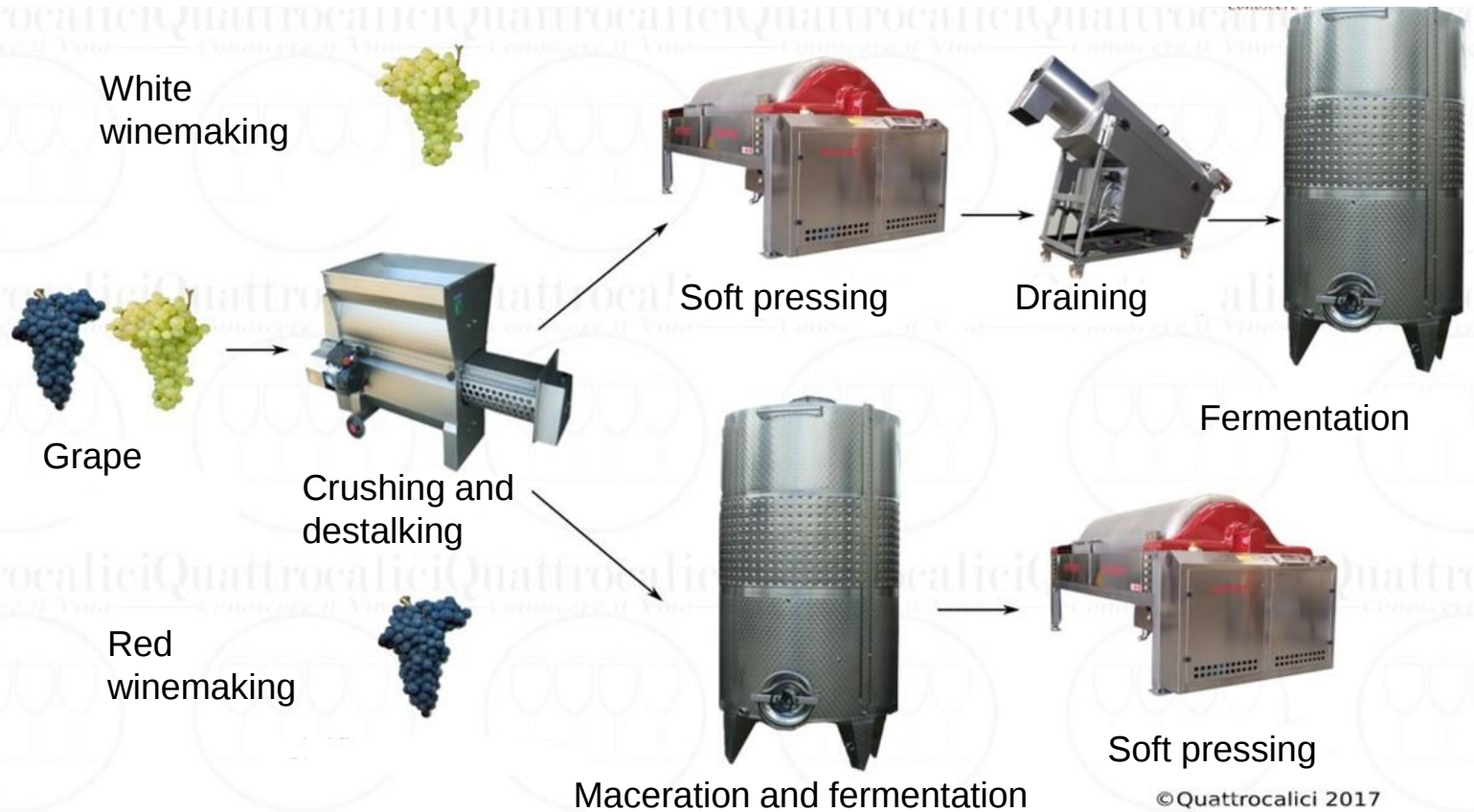
Bertinora and Vernaccia del viandante

Cavecchia and Albana rosa

Vernaccina



Winemaking processes



Mipaaf, D.M. 24 giugno 2008



Microvinification

Objective of the study

1. Metabolomic characterization of wines.
2. Metabolomic valorization of minor wines.
3. NMR characterization of aromatic white wines.
4. Finding of minor biomarker that can enhance the traceability of wines and that can be used to find potential adulterations.

Analytical approach

LC–MS Ion Trap

HPLC

Preliminary anthocyanins
analysis (2017)

GC–MS

Targeted volatile compounds
analysis (2017)

^1H -NMR (400 MHz)*

Untargeted characterization

UPLC–MS Q-Exactive (Orbitrap)

Targeted anthocyanins
analysis (2018 and 2019)

XCMS Online

Untargeted anthocyanins
analysis (2018 and 2019)

^1H -NMR (600 MHz)

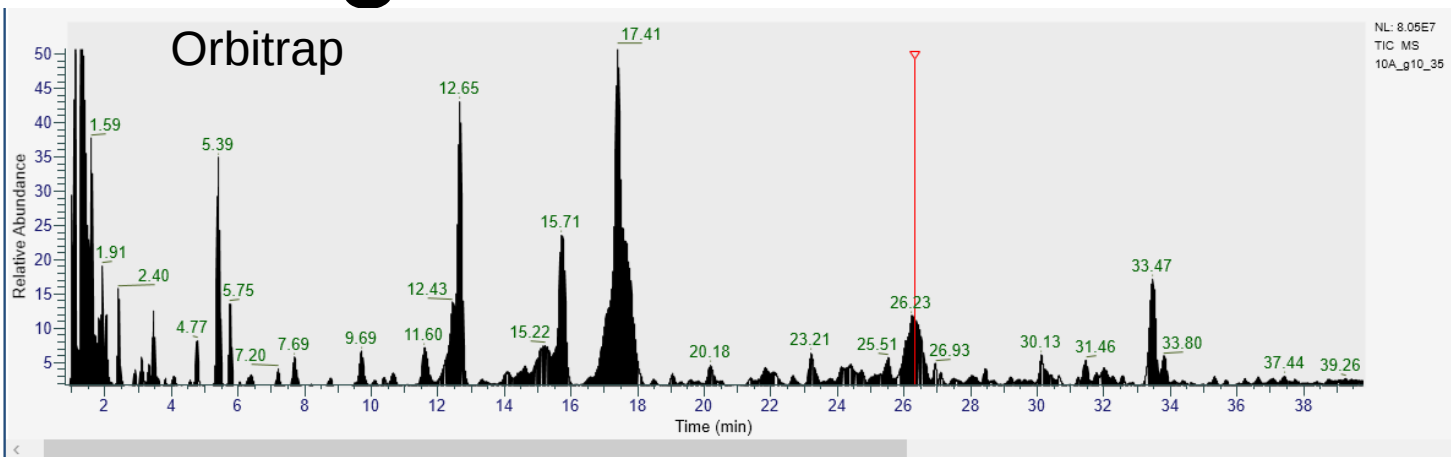
Untargeted analysis

^{13}C -NMR (600 MHz)

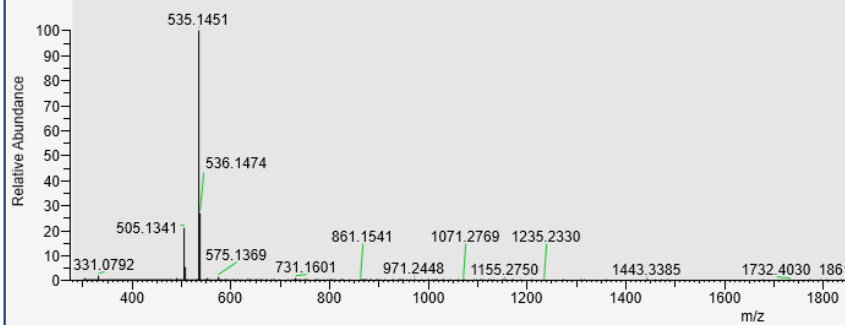
(2018 and 2019)

*Internship at University of Barcelona (2019)

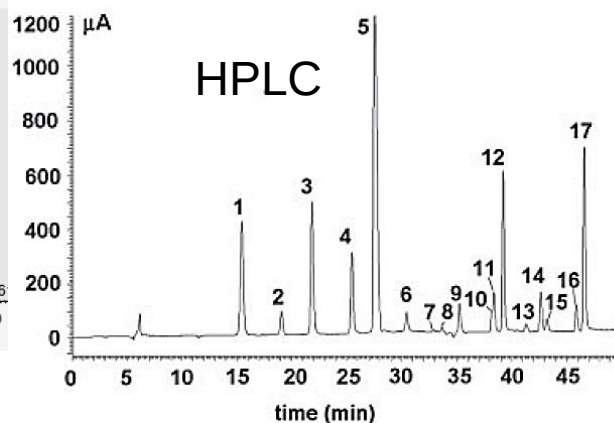
Targeted LC-MS results



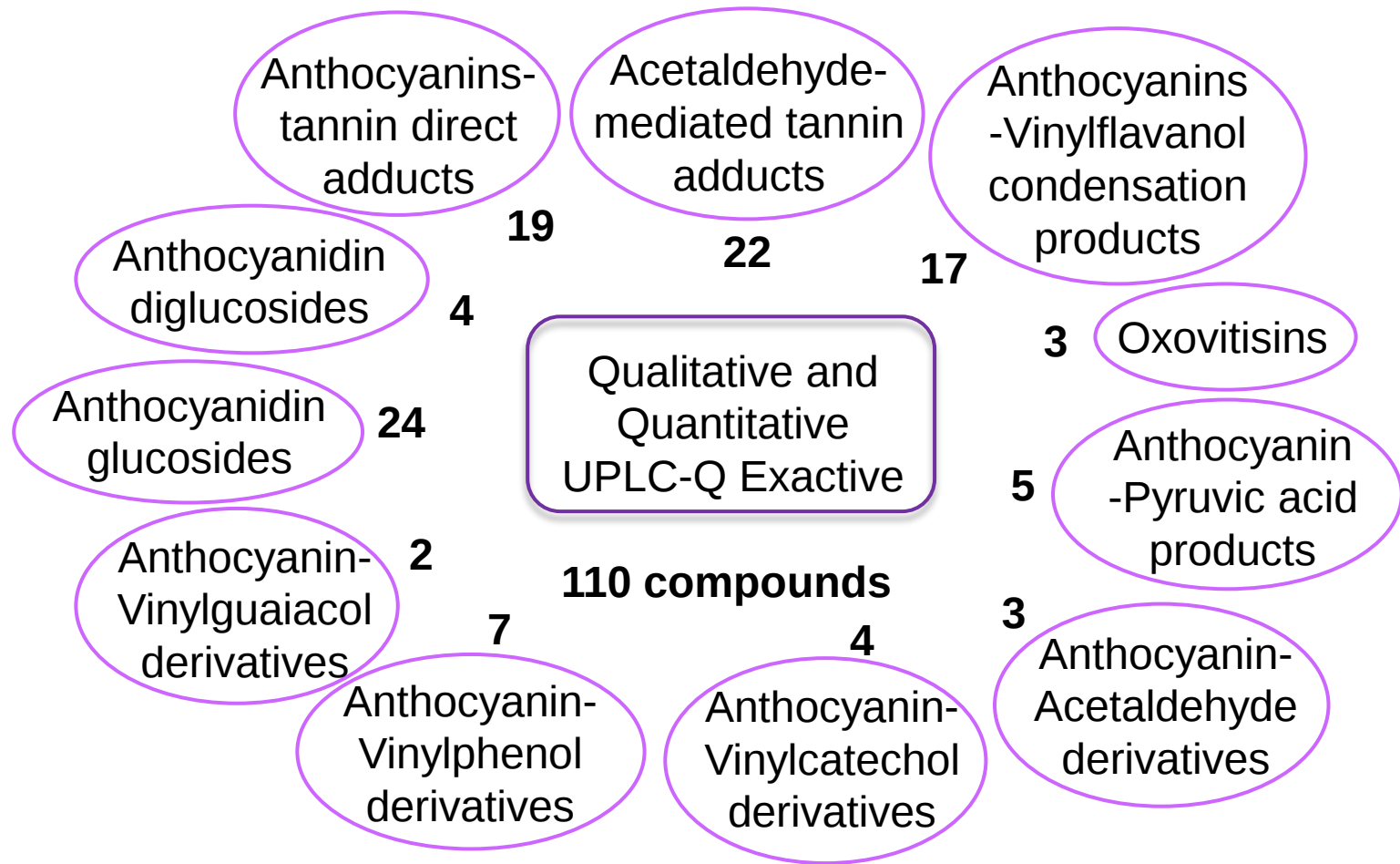
~Spectrum 1 5905 - 10A_g10_35 - C1T1
10A_g10_35 #5905 RT: 26.34 AV: 1 NL: 4.05E+006
T: FTMS + c ESI Full ms [300.0000-3000.0000]



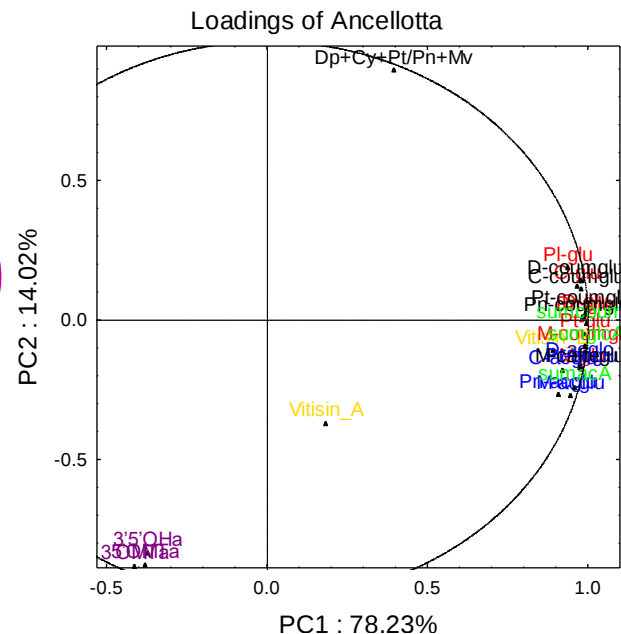
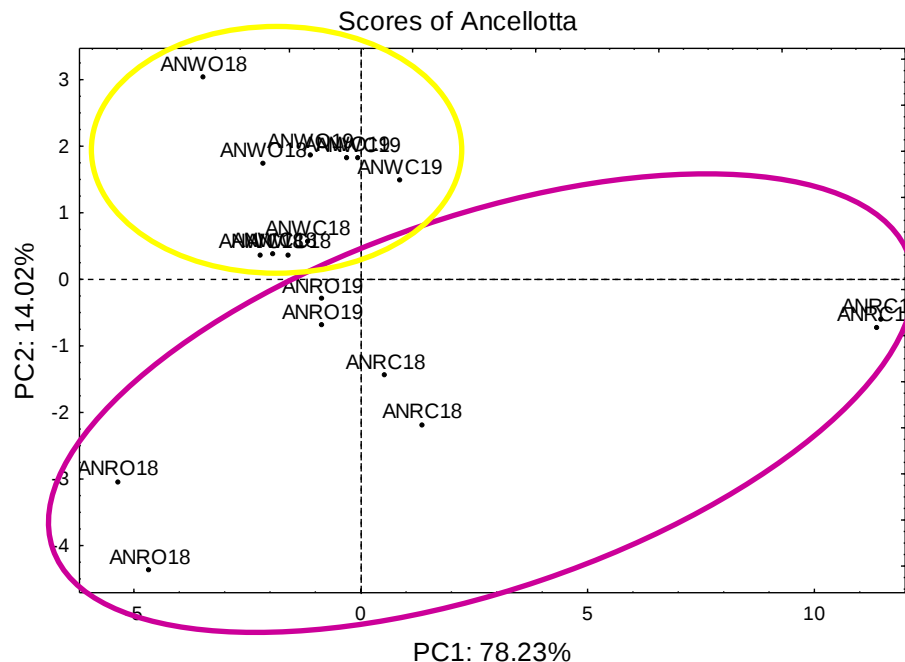
High mass accuracy: up to 3 ppm



Targeted LC-MS results



Ancellotta wines LC-MS results



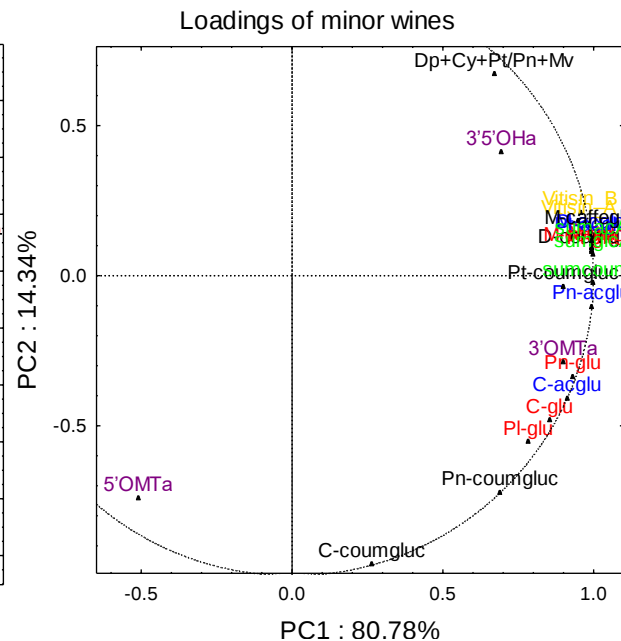
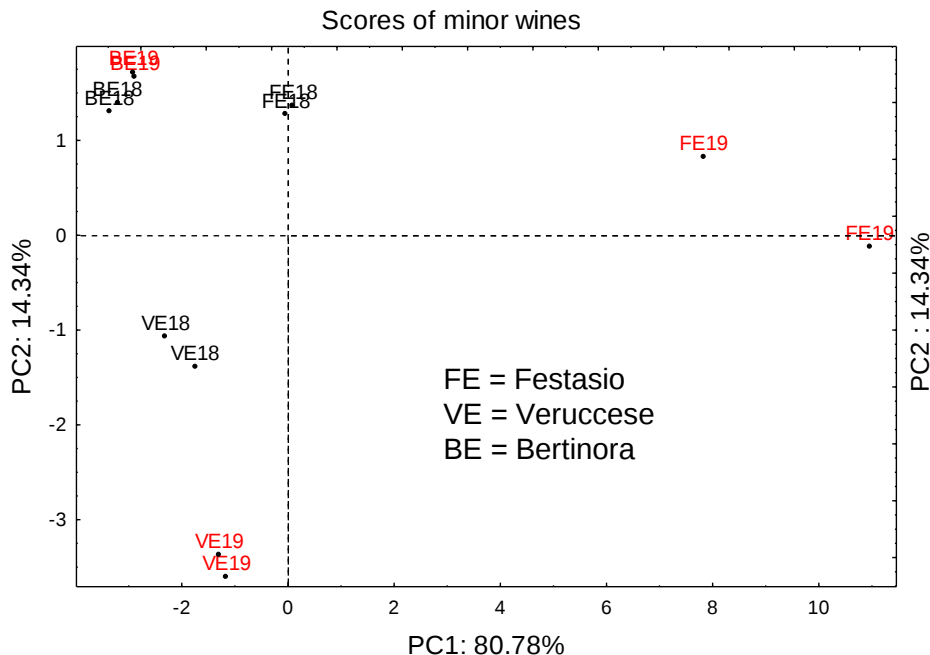
Delphinidin, Cyanidin, Petunidin, Pelargonidin, Peonidin, and Malvidin (-3-O-monoglucosides; -3-O-(6-acetyl)glucoside; -3-O-(6-p-coumaroyl)glucoside).

Vitisin A = Malvidin-3-glucoside pyruvic acid

Vitisin B = Malvidin-3-glucoside acetaldehyde

Sumglu = sum of all the -3-O-monoglucosides
 Summac = sum of all the -3-O-(6-acetyl)glucoside
 Sumcoum = sum of all the -3-O-(6-p-coumaroyl)glucoside
 3'5'OH = (Delph+Pet+Malv)/(Cyan+Peon)
 3'OMT = Peon/Cyan
 5'OMT = Malv/Delph
 Dp+Cy+Pt/Pn+Mv = (Delph+Cyan+Pet)/(Peon+Malv)

Minor wines LC-MS results



Delphinidin, Cyanidin, Petunidin, Pelargonidin, Peonidin, and Malvidin (**-3-O-monoglucosides**; **-3-O-(6-acetyl)glucoside**; **-3-O-(6-p-coumaroyl)glucoside**).

Vitisin A = Malvidin-3-glucoside pyruvic acid

Vitisin B = Malvidin-3-glucoside acetaldehyde

Sumglc = sum of all the -3-O-monoglucosides

Sumac = sum of all the -3-O-(6-acetyl)glucoside

Sumcoum = sum of all the -3-O-(6-p-coumaroyl)glucoside

3'5'OH = (Delph+Pet+Malv)/(Cyan+Peon)

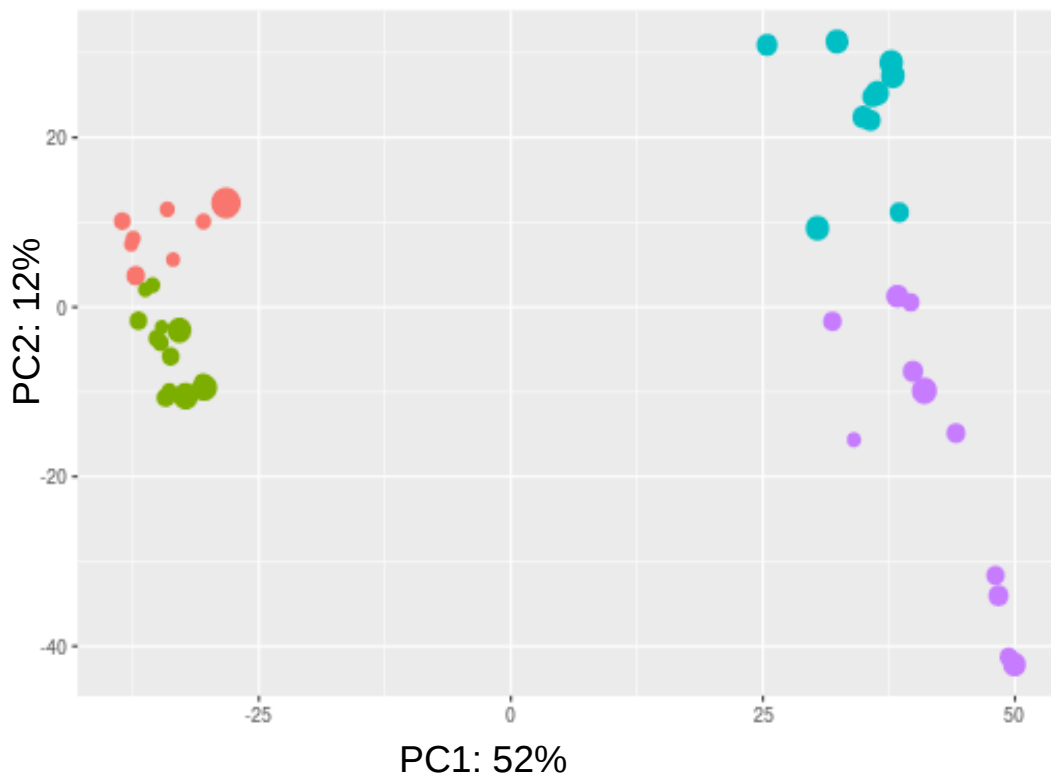
3'OMT = Peon/Cyan

5'OMT = Malv/Delph

Dp+Cy+Pt/Pn+Mv = (Delph+Cyan+Pet)/(Peon+Malv)

Untargeted LC-MS results

XCMS Online: 2616 compounds detected



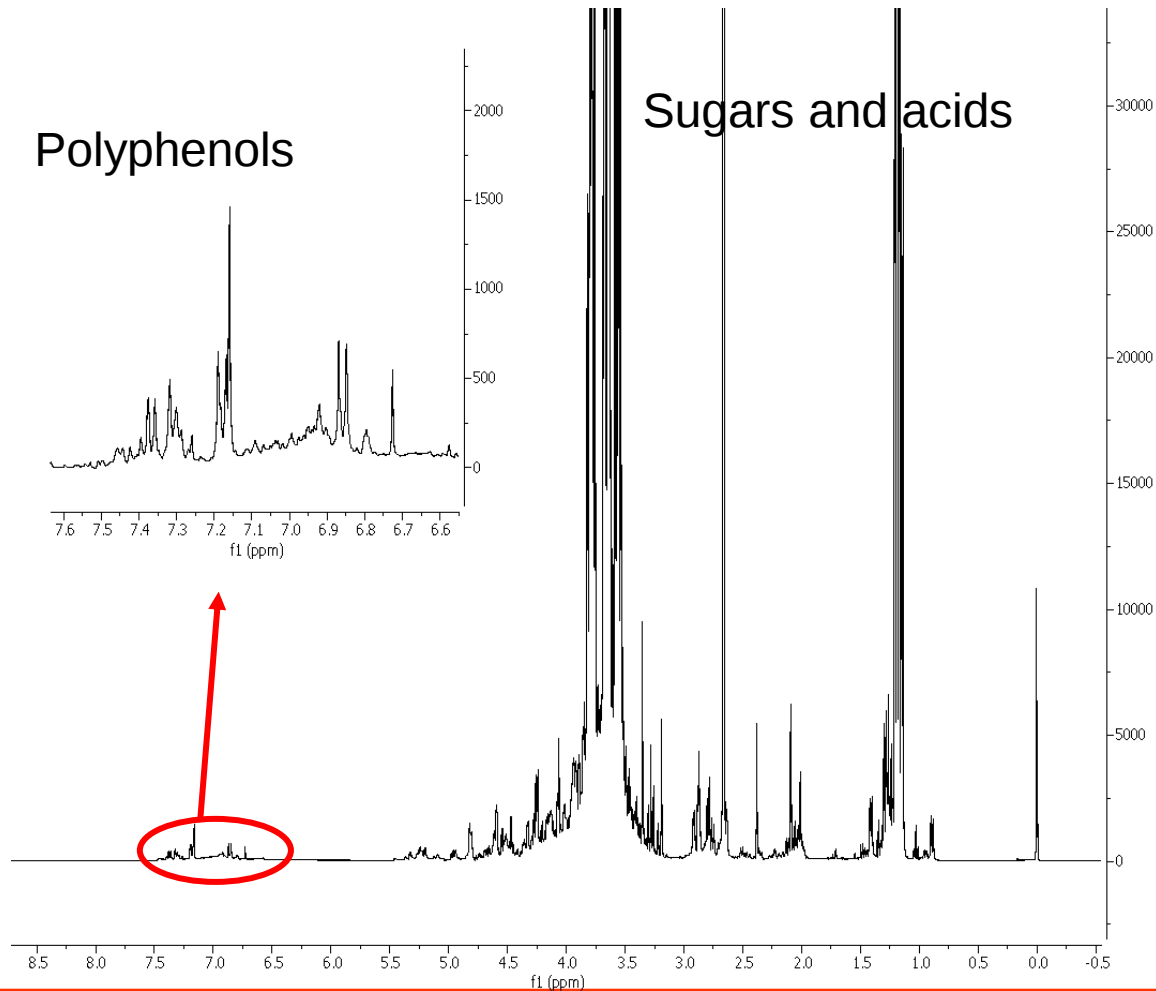
• Verucce, Bertinora, Rossiola, Festasio (2018)

• Ancellotta organic and conventional (2018)

• Verucce, Bertinora, Rossiola, Festasio, Termarina (2019)

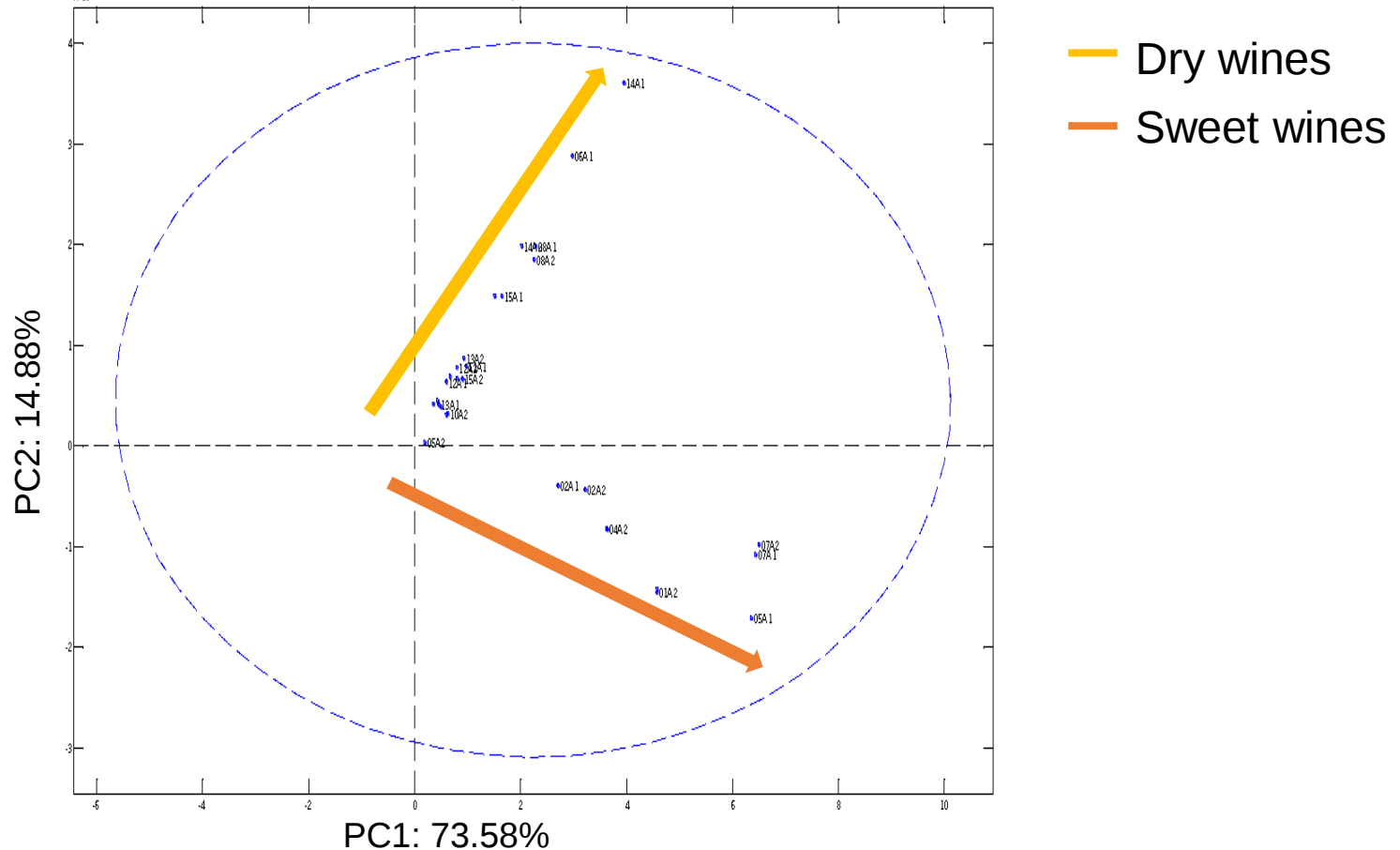
• Ancellotta organic and conventional (2019)

^1H -NMR 600 MHz results



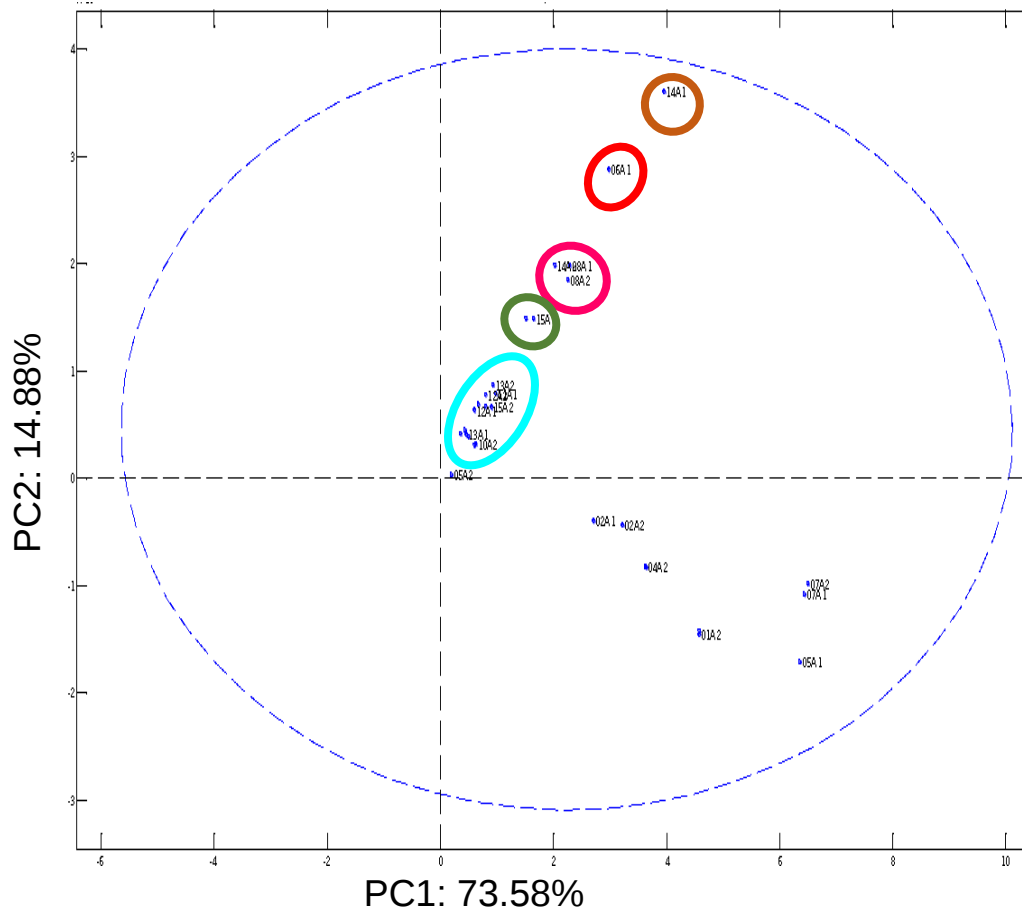
^1H -NMR 600 MHz results

Scores of Malvasia di Candia Aromatica



^1H -NMR 600 MHz results

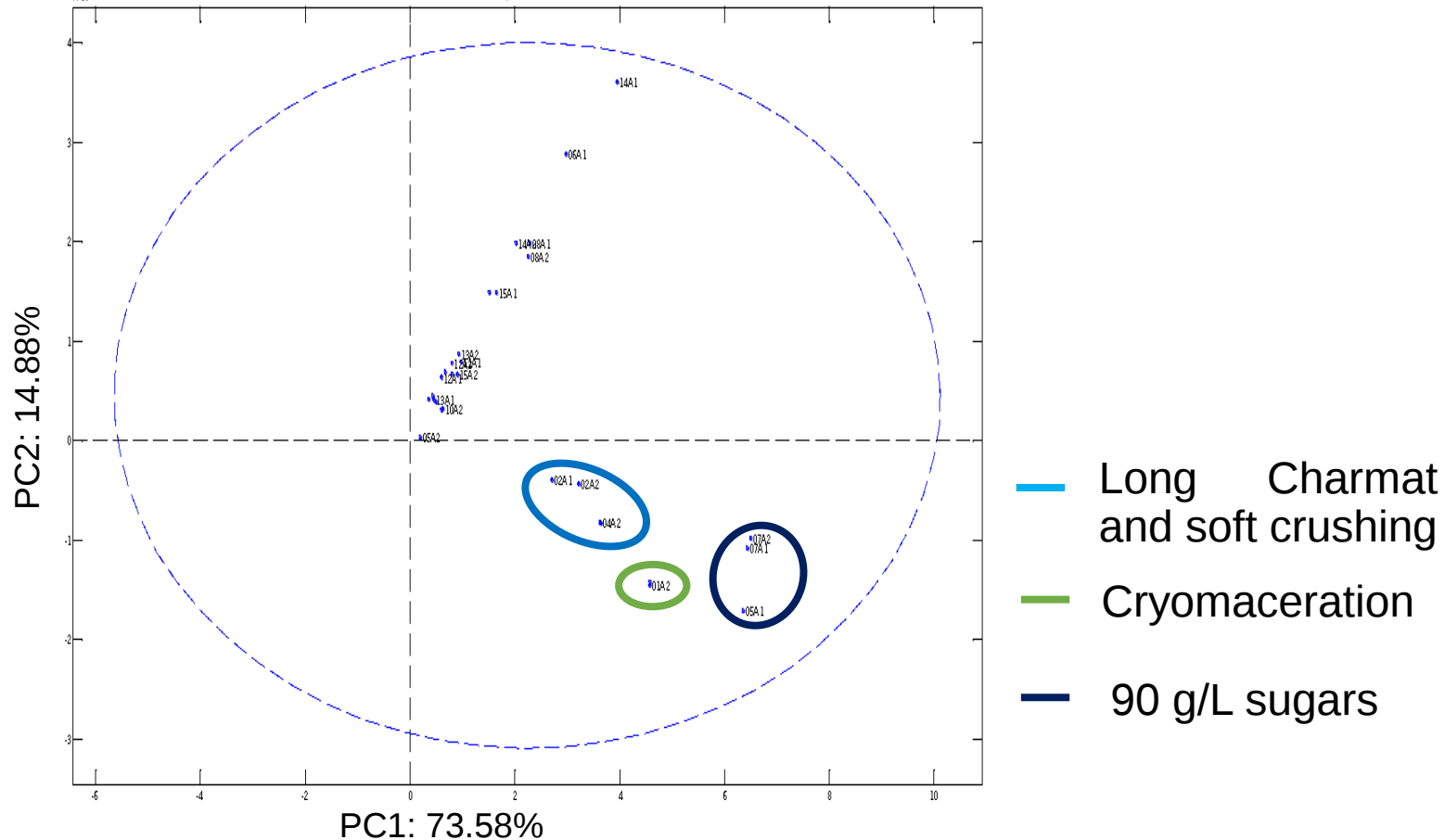
Scores of Malvasia di Candia Aromatica



- Long Charmat with bâtonnage
- 20% aged in barrels
- Short cryomaceration
- Short Charmat and long refining
- Short Charmat (20-30 days)

^1H -NMR 600 MHz results

Scores of Malvasia di Candia Aromatica



Conclusions

1. The minor wines can diversify the market.
2. Safeguarding the agricultural biodiversity heritage.
3. Several classes of anthocyanins can be used to study the properties, origin and adulteration of wine.
4. ^1H -NMR permits to discriminate wines according to their oenological practices and it is a promising approach for phenolic and volatile substances characterization.

Publications

Published during the “XIX giornata della chimica dell’Emilia-Romagna”, Modena, December 6th, 2019

ADVANCED CHARACTERIZATION TECHNIQUE FOR WINE

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Other Publications

Montevecchi, G., Setti, L., Olmi, L., Buti, M., Laviano, L., Antonelli, A., Sgarbi, E., 2019. Determination of Free Soluble Phenolic Compounds in Grains of Ancient Wheat Varieties (*Triticum* sp. pl.) by Liquid Chromatography–Tandem Mass Spectrometry. *J. Agric. Food Chem.* 67, 201-212.

Caradonia, F., Setti, L., Hagassou, D., Buti, M., Giaretta Azevedo, C.V., Laviano, L., Bezzi, G., Francia, E., Ronga, D. Innovative Fertilizers to Improve Sustainability and Productivity of Processing Tomato. ESA 2018, XV European Society for Agronomy Congress, August 27-31, 2018, Geneva, Switzerland. PS-10.2-04

Ronga, D., Setti, L., Salvarani, C., De Leo, R., Bedin, E., Pulvirenti, A., Milc, J., Pecchioni, N., Francia, E., 2018. Effects of solid and liquid digestate for hydroponic baby leaf lettuce (*Lactuca sativa* L.) cultivation. *Sci. Hort.* 244, 172-181.

Setti, L., Francia, E., Pulvirenti, Francia, E., Gigliano, S., Zaccardelli, M., Pane, C., Caradonia, F., Bortolini, S., Maistrello, L., Ronga, D., 2019. Use of black soldier fly (*Hermetia illucens* (L.), Diptera: Stratiomyidae) larvae processing residue in peat-based growing media. *Waste Manag.* 95, 278–288.

Caradonia, F., Francia, E., Barbieri, R., Setti, L., Hagassou, D., Ronga, D., 2020. Interspecific rootstock can enhance the yield of processing tomato (*Solanum lycopersicum* L.) in the organic farming. *Biol. Agric. Hort.*

Other Publications

Setti, L., Francia, E., Pulvirenti, A., De Leo, R., Martinelli, S., Maistrello, L., Macavei, L.I., Montorsi, M., Barbi, S., Ronga, D., 2020. Bioplastic Film From Black Soldier Fly Prepupae Proteins Used As Mulching: Preliminary Results. *Agronomy*, 10, 933.

Bortolini, S., Macavei, L.I., Hadj Saadoun, J., Foca, G., Ulrici, A., Bernin, F., Malferrari, D., Setti, L., Ronga, D., Maistrello, L., 2020. *Hermetia illucens* (L.) larvae as as chicken manure management tool for circular economy. *J. Clean. Prod.* 262, 121289.

Future perspectives

1. *Ad hoc* further studies are necessary to evaluate the role and the origin of minor secondary metabolites.
2. Further metabolomic studies are crucial to understand the relationship among wine quality, agronomical practices, environmental conditions and genetical characters.
3. Comparison with commercially established wines.

Future perspectives

Setti, L., Montevecchi, G., Masino, F., Nigro, G., Antonelli, A., 2020. Anthocyanin metabolomics of northern Italy wines through LC-MS-HESI-ORBITRAP. In print

Setti, L., Montevecchi, G., Masino, F., Bertelli, D., Antonelli, A., 2020. Characterization of different Malvasia wines by NMR spectroscopy. In print

Acknowledgement



dott. Giovanni Nigro



dott. Fabrizio Bocedi

dott. Stefano Giovannini



dott. Franco Roccatello



prof. Cristina Minguillón

prof. Elvira López Tamames



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Food Chemistry and Technology

*“Et però credo che molta felicità sia agli homini
che nascono dove si trovano i vini buoni”.*

Leonardo da Vinci



PhD student
Leonardo Setti