

How wine polyphenols evolve during wine ageing ?

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Outline

I. Introduction to phenolic compounds of grapes and wine and their evolution during wine ageing

II. Example of degradation reaction involving Malvidine-3-O-glucoside

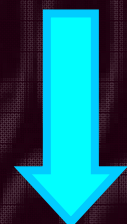
III. Example of Polymerization of tannins involving acetaldehyde

IV. Conclusion

Storage of wine (O_2 , H^+ , T°)



Phenolic compounds



Physico-chemical transformations

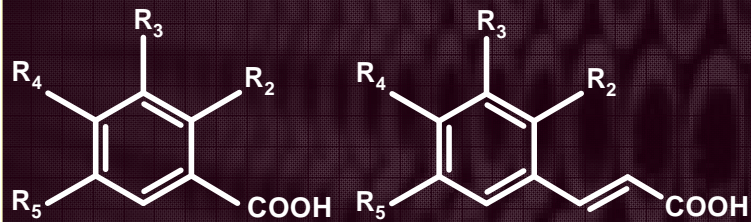


Taste and color changes

Phenolic compounds in grape and wine

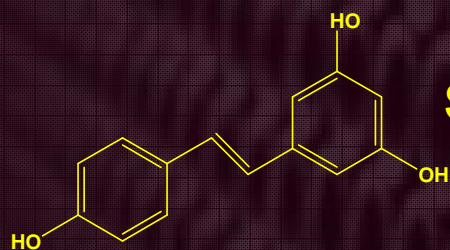
Non-flavonoids

Phenolic acids



Benzoic acids

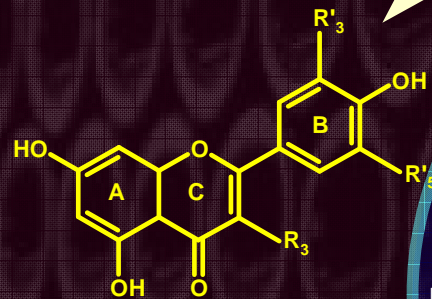
Cinnamic acids



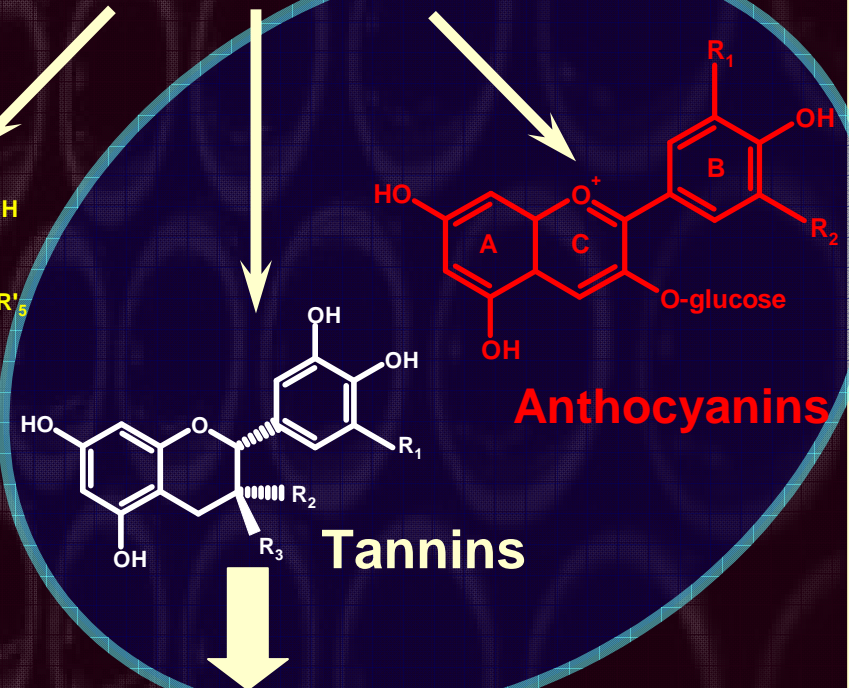
Stilbens

➤ Taste and color of wines

Flavonoids

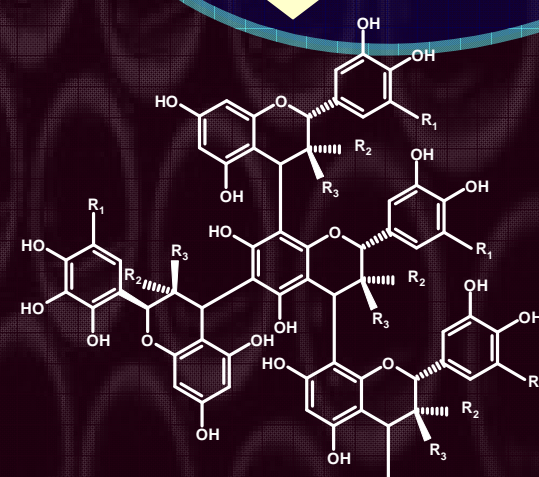


Flavonols

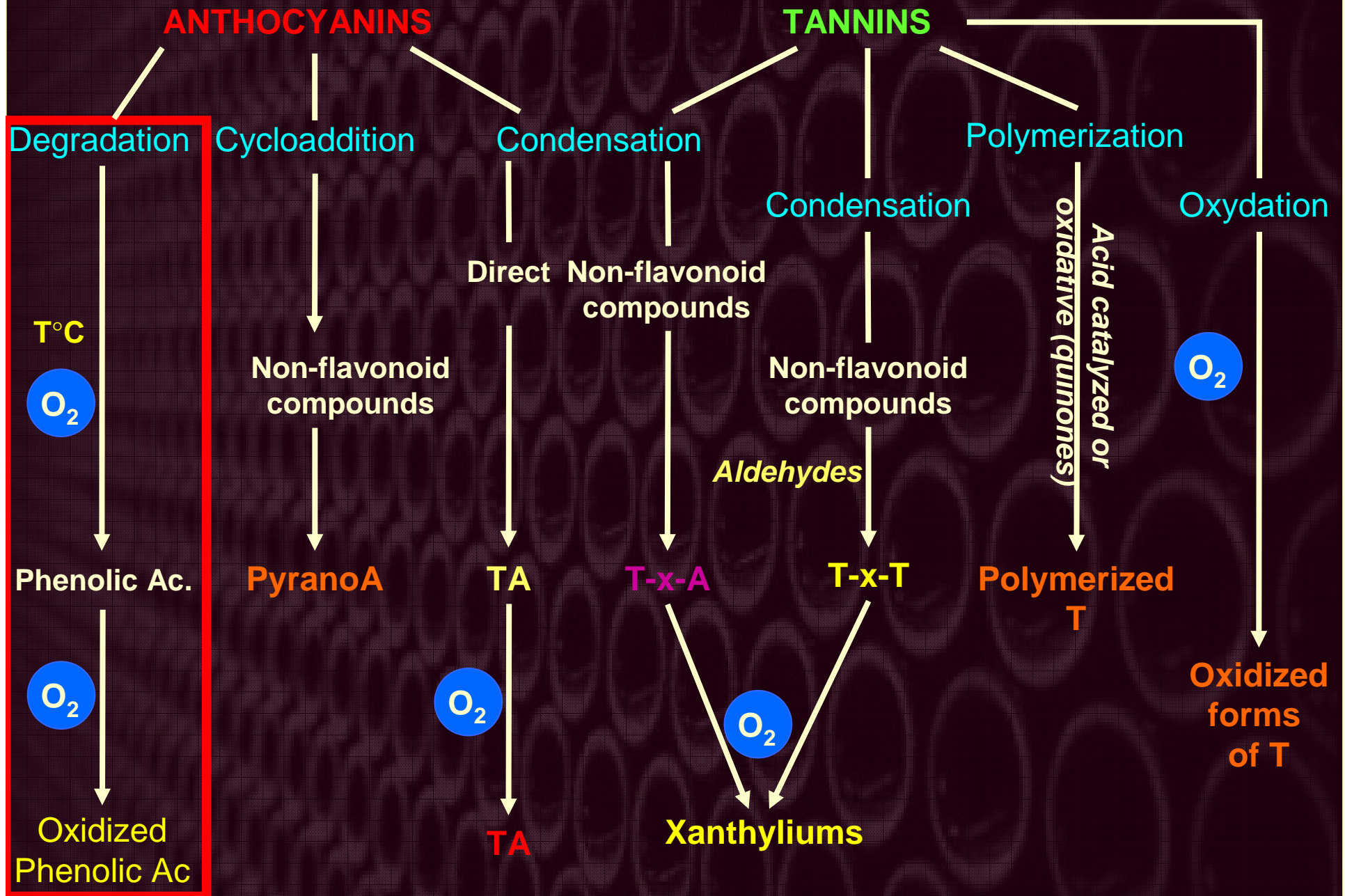


Anthocyanins

Tannins



Reactions involving tannins and anthocyanins



II

Example of degradation reaction

involving

Malvidine-3-O-glucoside



I. Study of Malvidin-3-O-glucoside degradation

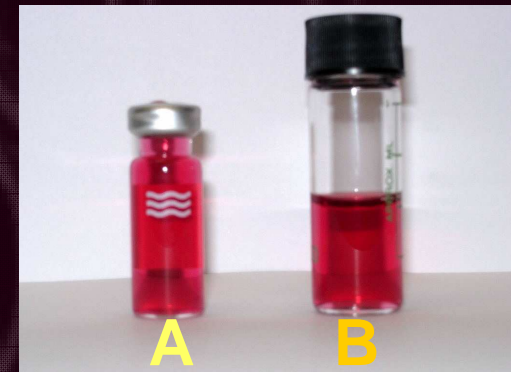
Objective:

1. Effect of O₂:

- Study of oxidoreduction state markers

Protocole:

- Model wine solution (12% EtOH, 5 g.L⁻¹ Tartaric acid, pH 3,4)
- Malvidine-3-O-glucoside (250 mg/L)
 - Low O₂, (control flushed with Nitrogen)(A)
 - O₂ rich (excess 450 mg/L d' O₂) (B)
- 90°C during 24 hours



HPLC/UV-Vis/MS

NMR

I. Study of Malvidin-3-O-glucoside degradation

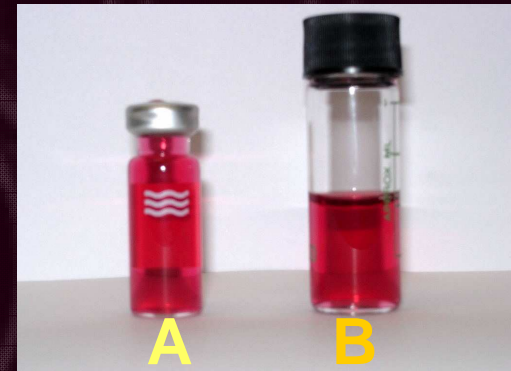
Objective:

1. Effect of O_2 :

- Study of oxidoreduction state markers

Protocole:

- Model wine solution (12% EtOH, 5 g.L⁻¹ Tartaric acid, pH 3,4)
- Malvidine-3-O-glucoside (250 mg/L)
 - Low O_2 , (control flushed with Nitrogen)(A)
 - O_2 rich (excess 450 mg/L d' O_2) (B)
- 90°C during 24 hours



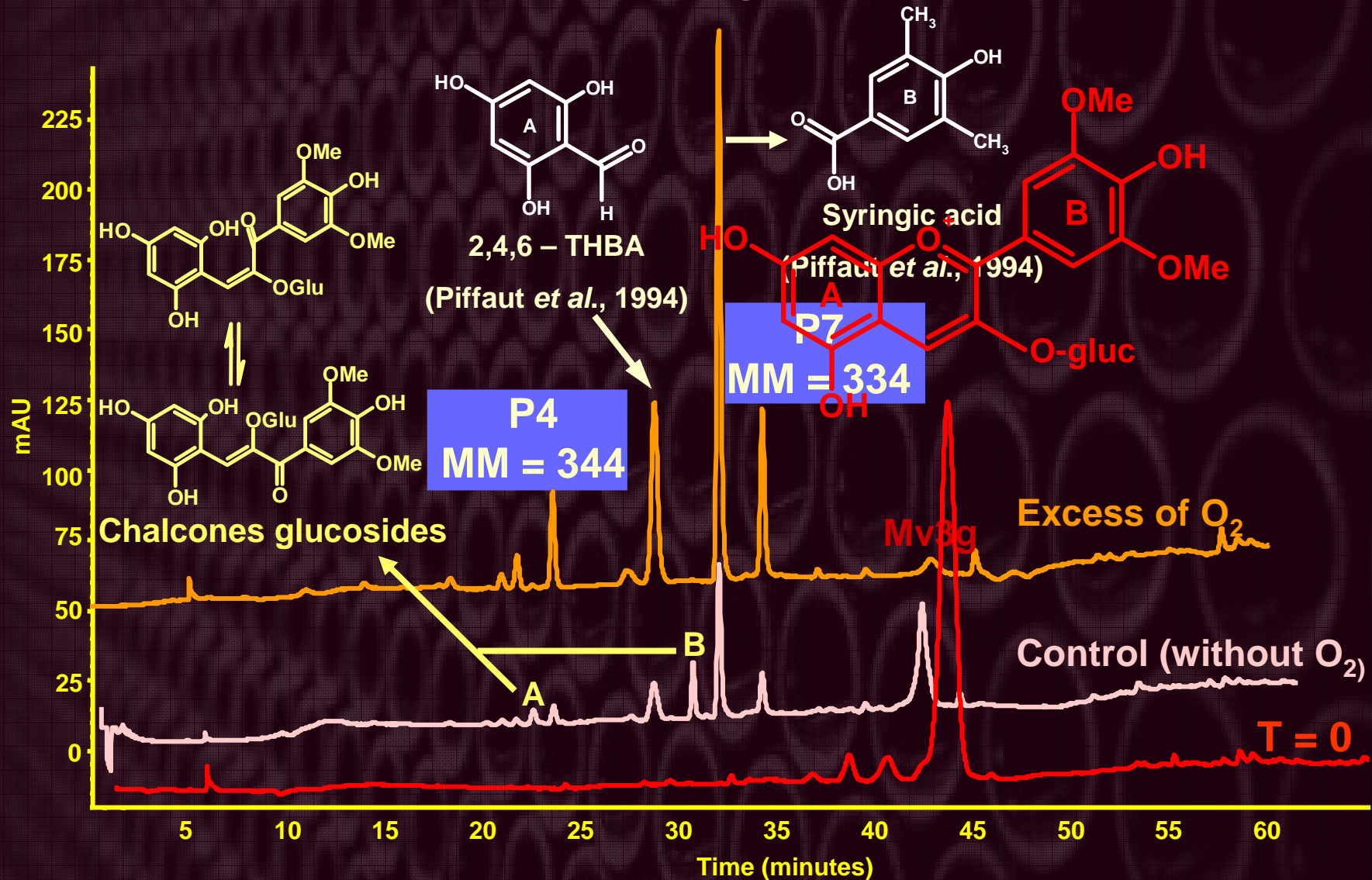
HPLC/UV-Vis/MS

NMR

I. Study of Malvidin-3-O-glucoside degradation

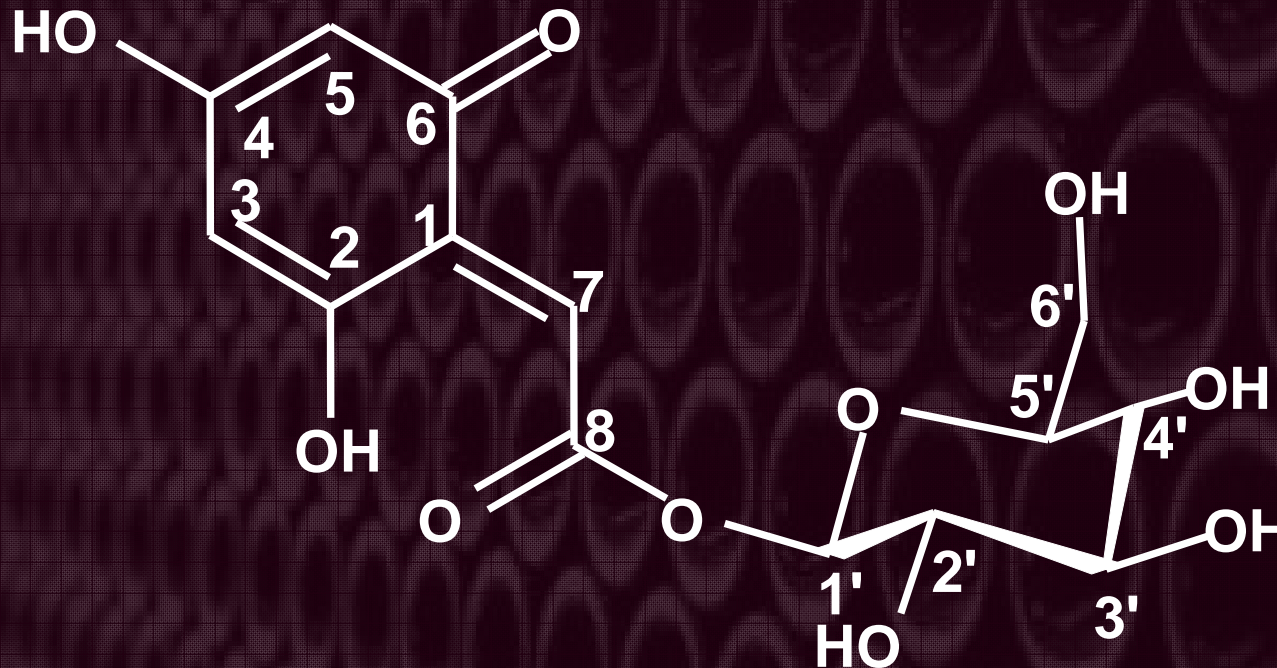
1. Effect of O₂ on Mv3g degradation (pH 3,4)

▪ HPLC / UV (280 nm) follow up during 24 hours



I. Study of Malvidin-3-O-glucoside degradation

- P4 by NMR (^1H , Cosy ^1H - ^1H , HSQC ^1H - ^{13}C)



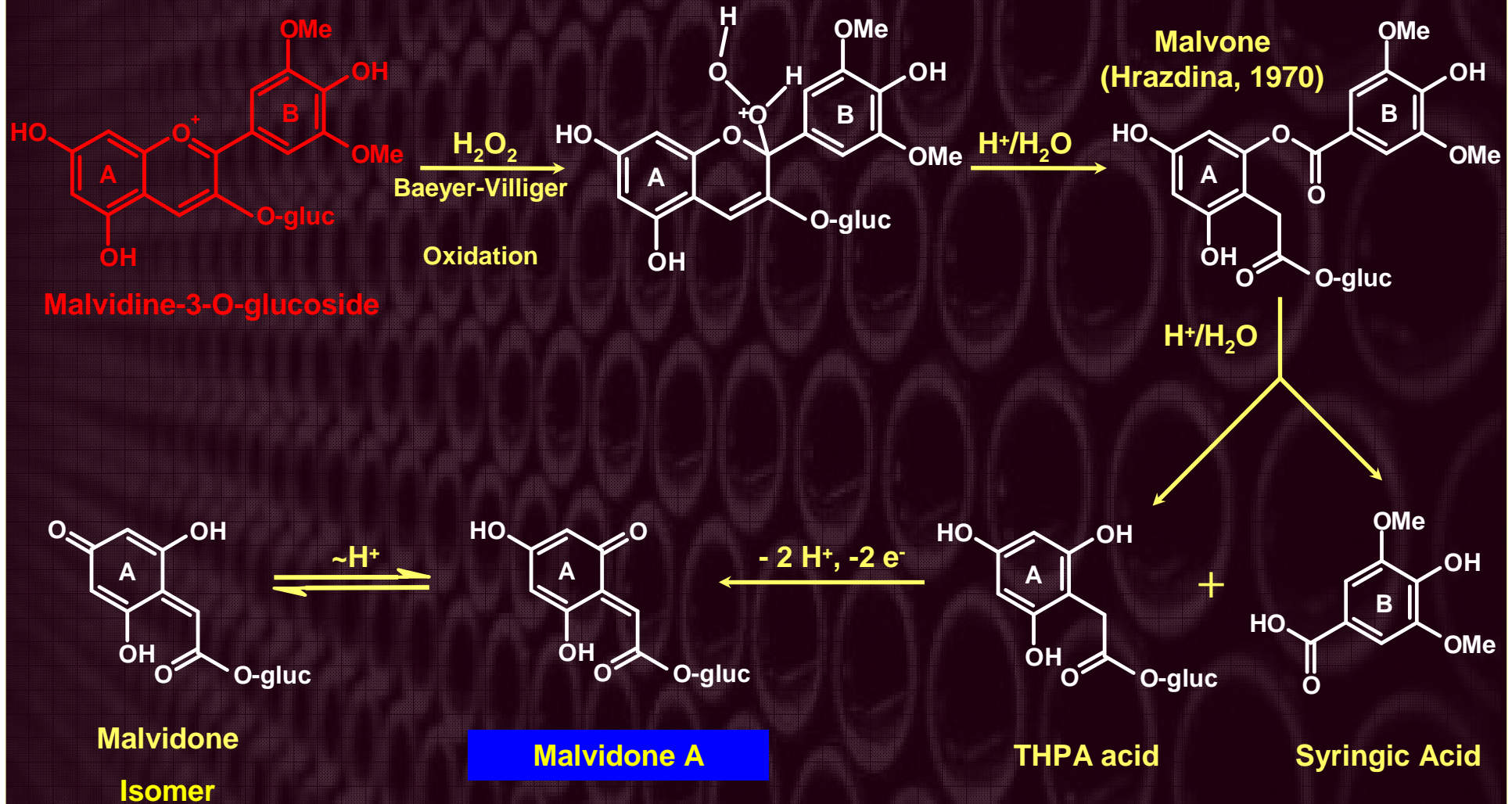
8- β -D-glucopyranosyl-2,4-dihydroxy-6-oxo-cyclohexa-2,4-dienylidene acid

Anthocyanidone A

Lopes, P.; Richard, T.; Saucier, C.; Teissedre, P.-L.; Monti, J.-P.; Glories, Y.
Anthocyanone A: A Quinone Methide Derivative Resulting from Malvidin 3-O-Glucoside Degradation
J. Agric. Food Chem., 2007, 55, 2698-2704.

I. Etude des réactions de dégradation de la Malvidine-3-O-glucoside

Proposed mechanism for Anthocyanidone A formation

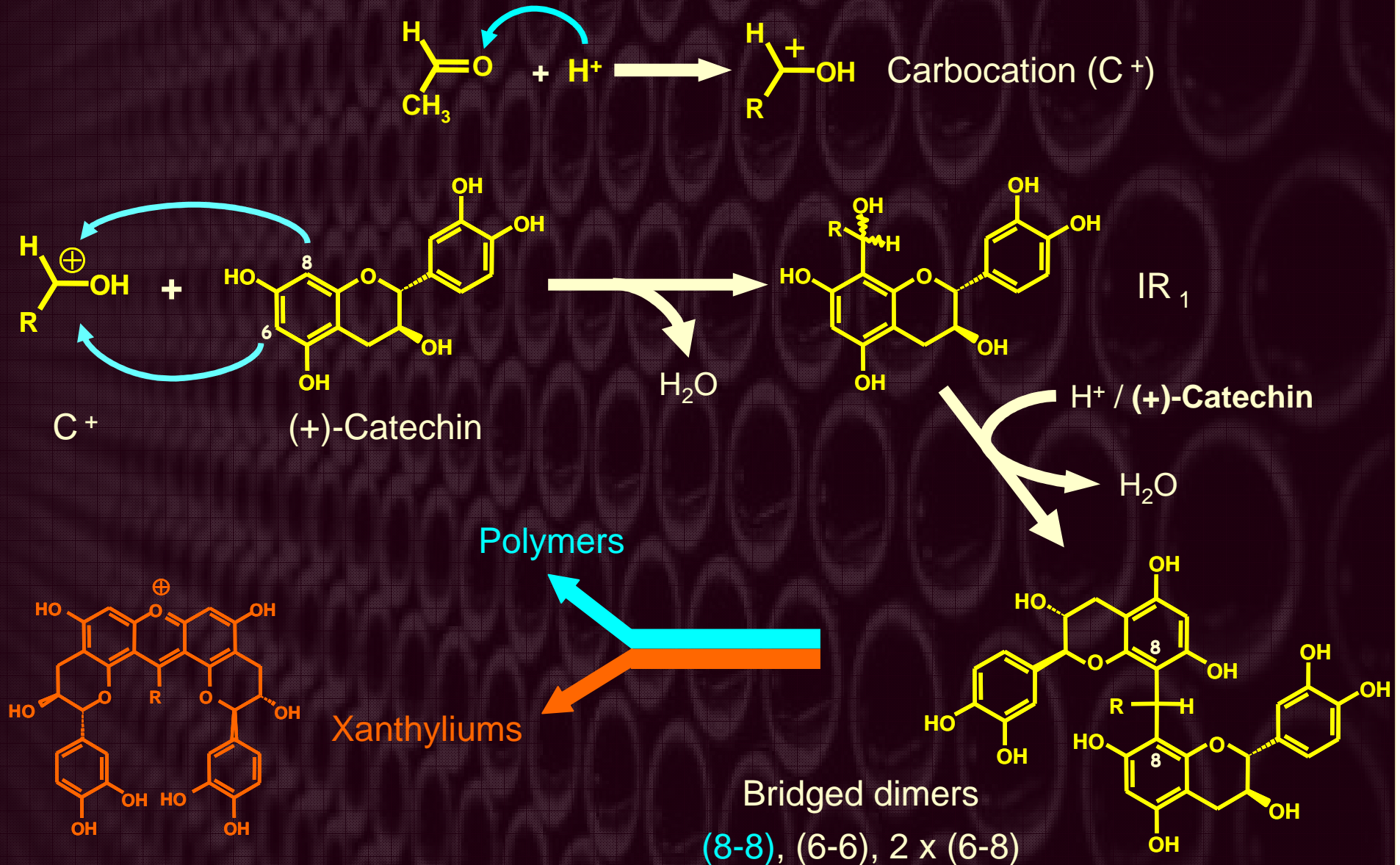




**Example of Polymerization of
tannins involving acetaldehyde**

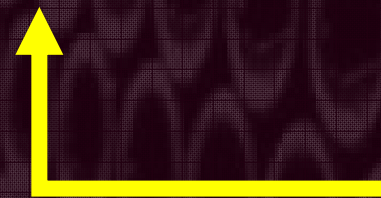
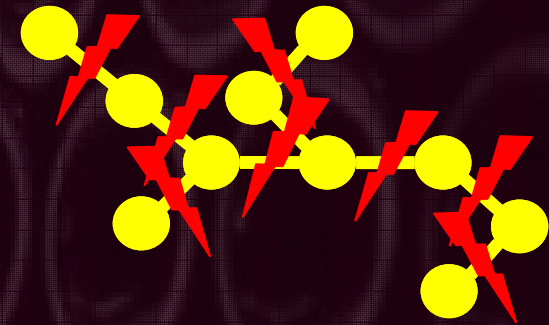
Mechanism of flavanol-Acetaldehyde polymerization

Mechanism is known and proven to occur in wine (Saucier *et al.*, 1997; Fulcrand *et al.*, 1997; ...)



Flavan-3-ol quantification

- Flavan-3-ol polymers
 - Structural complexity
 - Analytical technique limited
- Quantification based on polymer cleavage
- 2 methods
 - Thiolysis (Betts *et al.*, 1967; Rigaud *et al.*, 1991)
 - Phloroglucinolysis (Kennedy *et al.*, 2001; Peyrot des Gachons *et al.*, 2003)

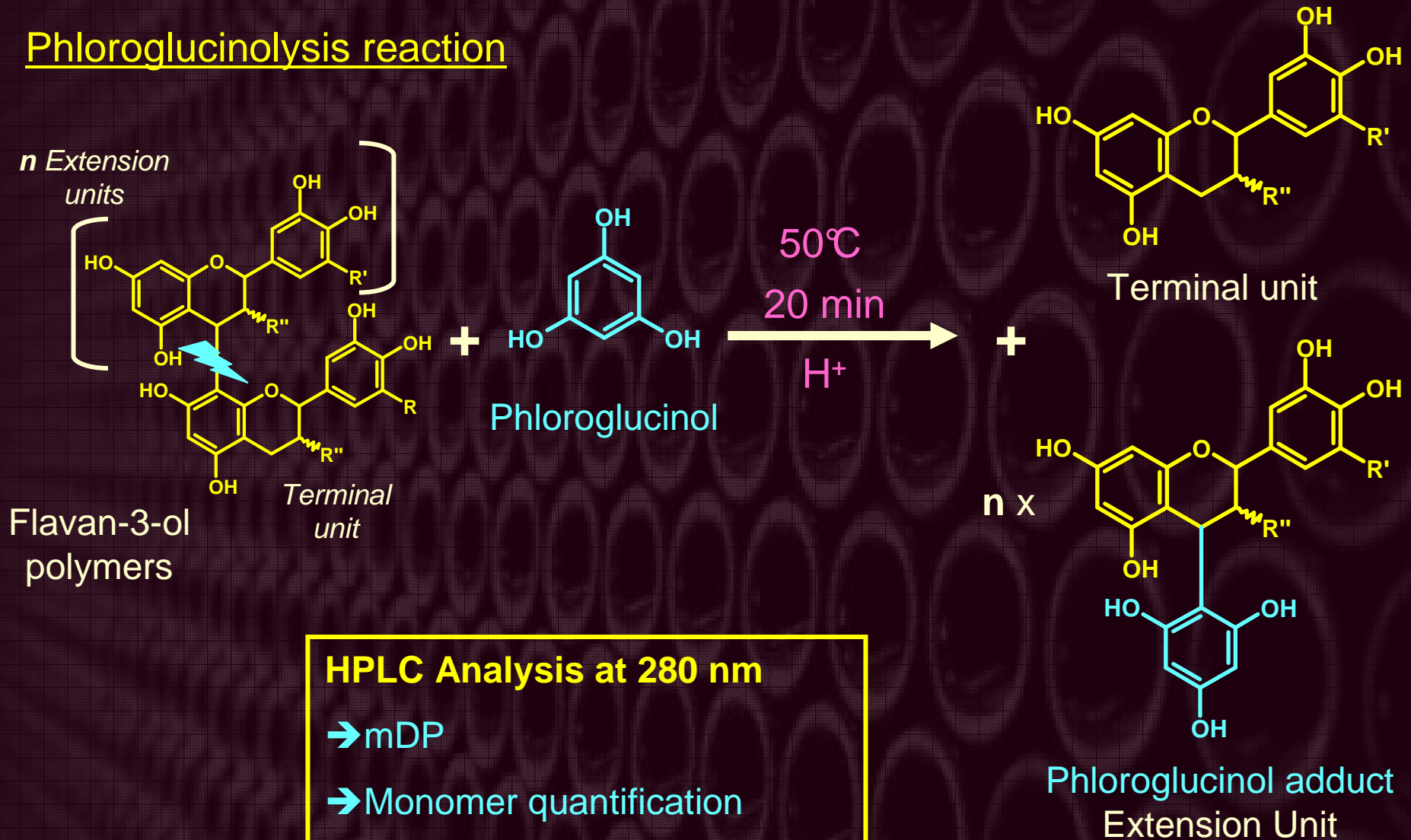


Work choice

Phloroglucinol odorless and non-toxic / benzylmercaptan

Analysis of ethylidene-bridged flavan-3-ols in red wine

Phloroglucinolysis reaction



HPLC Analysis at 280 nm

→ mDP

→ Monomer quantification

- Terminal units
- Extension units

Phloroglucinolysis of (+)-catechin ethylidene-bridged oligomers

1° (+)-catechin ethylidene-bridged oligomer synthesis

→ (+)-catechin-acetaldehyde condensation

- Excess of aldehyde
- Winelike solution and 40°C

→ Ethylidene-bridged oligomers

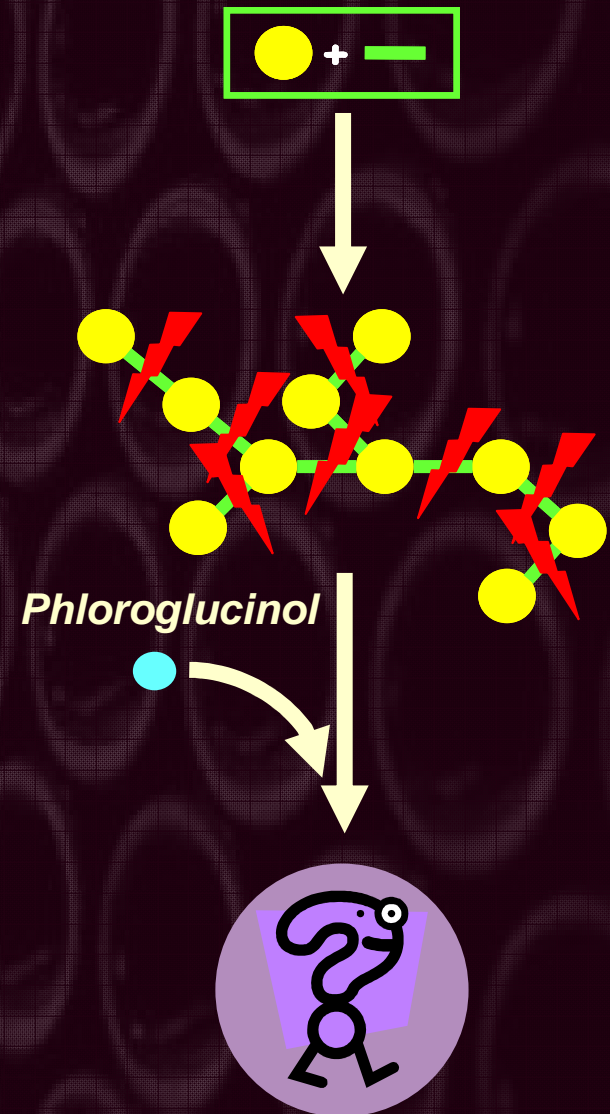
→ Monomer

→ Dimers, Trimers

2° Phloroglucinolysis

- Oligomers in phloroglucinolysis reactant
- 20 min at 50°C

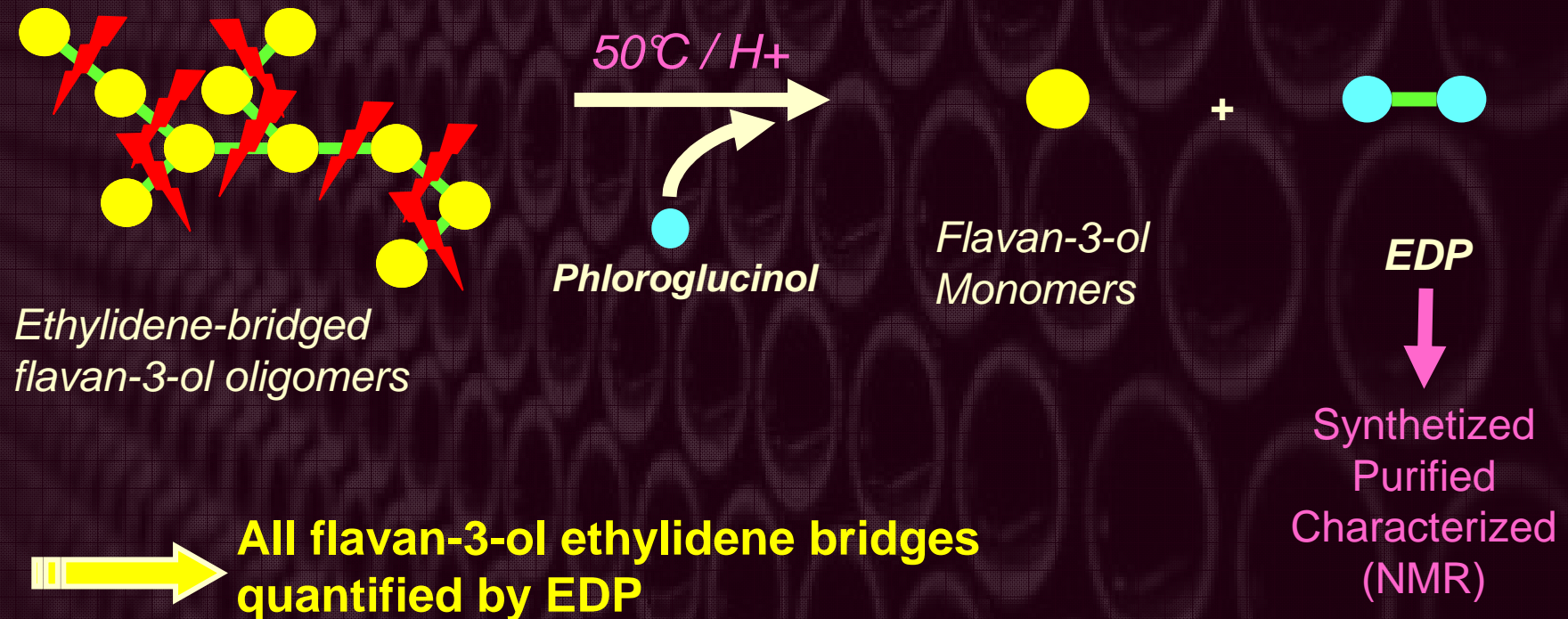
→ LC-MS and 280 nm analyses



Ethylidene-bridged flavan-3-ol phloroglucinolysis

→ Phloroglucinolysis

- Flavan-3-ol monomers released
- Ethylidene bridges captured by phloroglucinol : EDP



Quantification of flavan-3-ol ethylidene bridges in wine

1° SPE C₁₈: Purification / Concentration

2° Phloroglucinolysis

3° LC-MS Analysis



Method repeatability: 9.2%

Method recovery: 83% to 90% depending on ethylidene bridges conc.

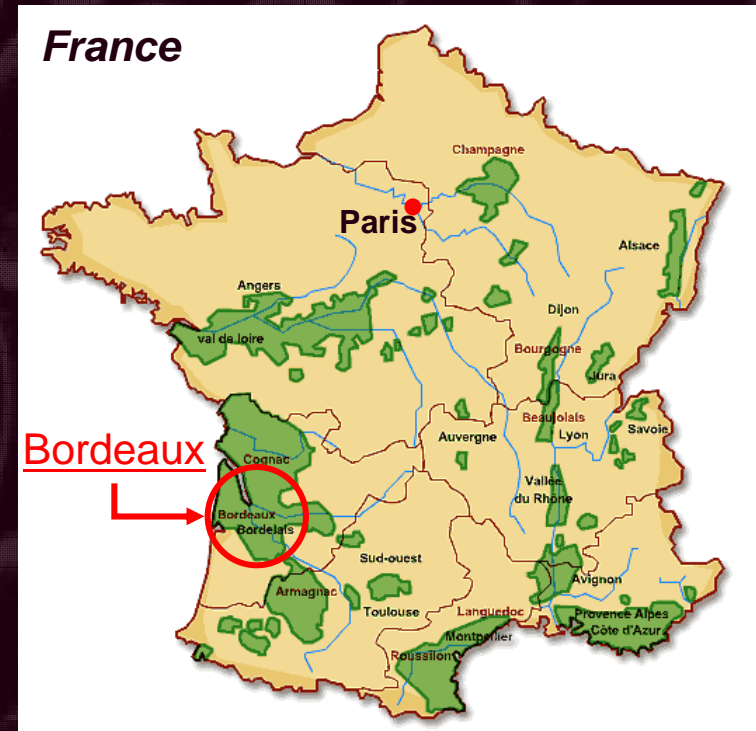
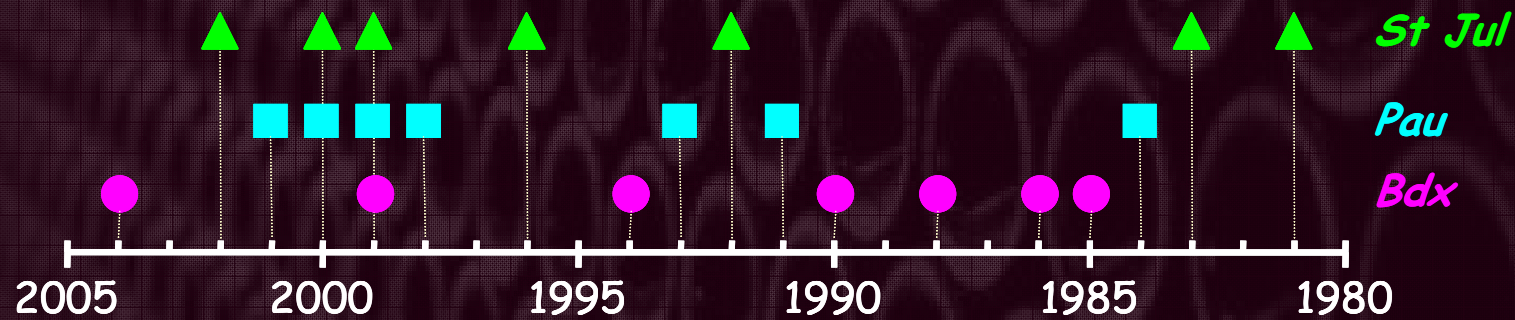
Analysis of ethylidene-bridged flavan-3-ols in red wine

Application to 21 red wines from Bordeaux area

– 3 Wineries in

- ● Bordeaux (Bdx)
- ■ Pauillac (Pau)
- ▲ Saint Julien (St Jul)

– Different vintages

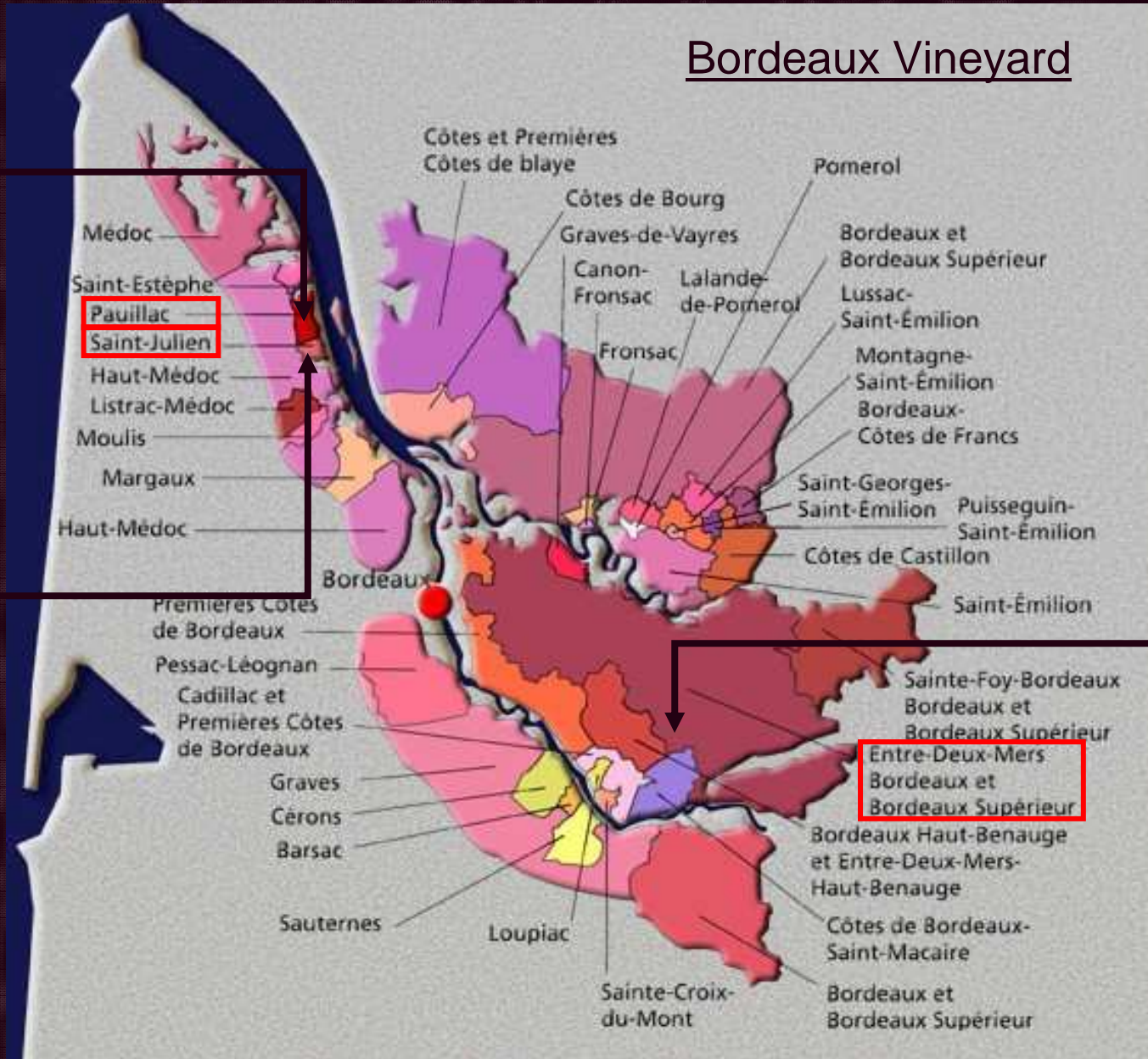


Analysis of ethylidene-bridged flavan-3-ols in red wine

Bordeaux Vineyard

Pauillac

Saint
Julien



Bordeaux

Analysis of ethylidene-bridged flavan-3-ols in red wine

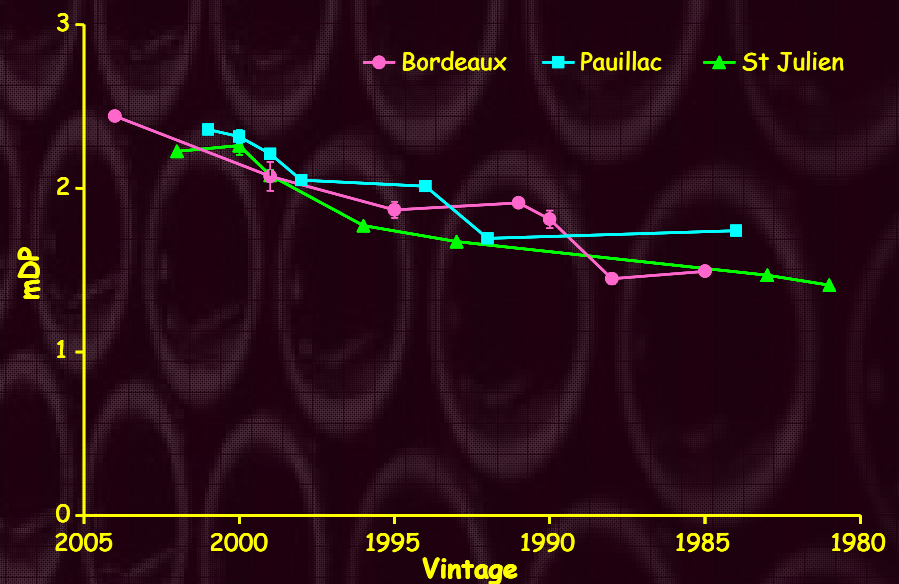
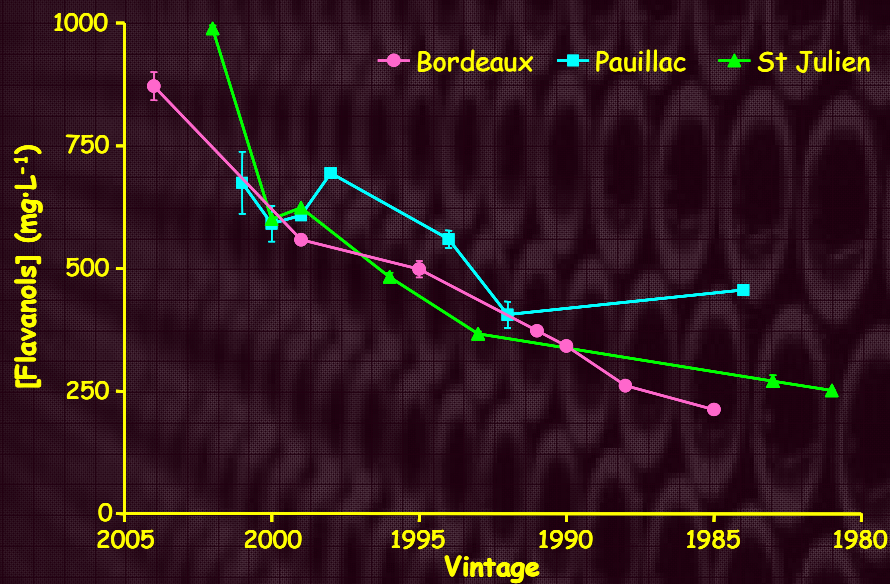
Analyses

- Flavan-3-ol contents

- ↘↘ Flavan-3-ols (FI)
- ↘ mDP

↘↘ With wine age

→ Rearrangement reactions with other wine compounds



Analysis of ethylidene-bridged flavan-3-ols in red wine

Analyses

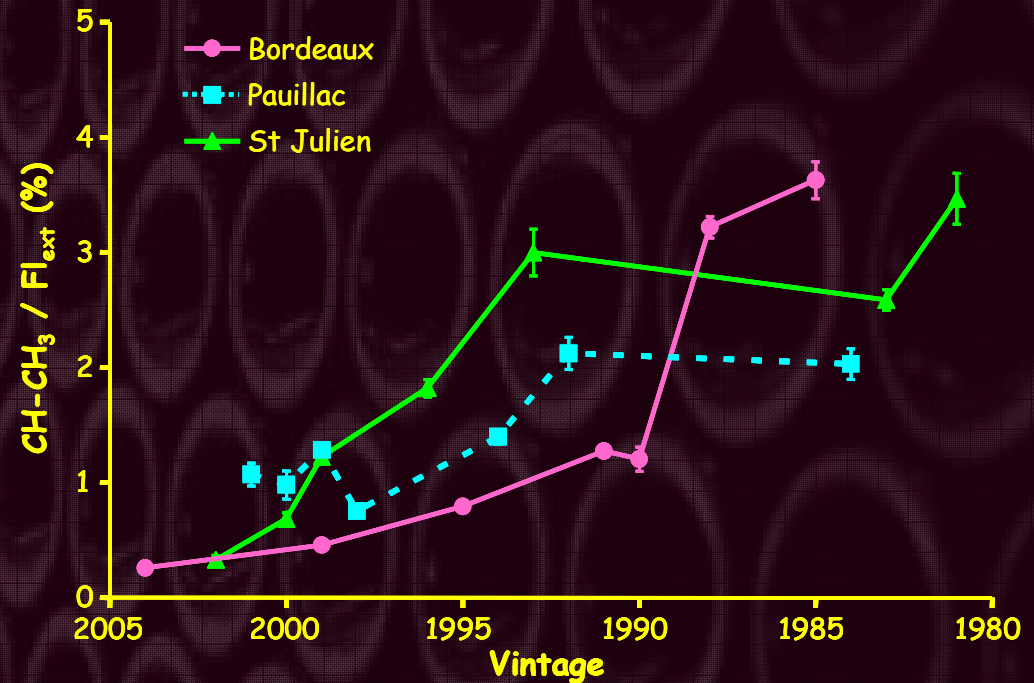
- % of Ethylidene bridges

• $\text{CH-CH}_3 / \text{Fl}_{\text{ext}}$

→ Low proportion

→ But ↗ with wine age

→ New index of wine aging ?



Conclusions

- First quantification of flavan-3-ol ethylidene bridges
 - EDP phloroglucinolysis
 - LC-MS analysis

- Proportion of Flavan-3-ol ethylidene bridges
 - Correlated with wine age
 - Could be a new marker for wine age or help in wine oxidation management (O₂ management)

Conclusions

- Drinkine, J.; Lopes, P.; Kennedy, J. A.; Teissedre, P.-L.; Saucier, C. Analysis of ethylidene-bridged flavan-3-ols in wine. *J. Agric. Food Chem.*, **2007** ,55, 1109 -1116
- Drinkine, J.; Lopes, P.; Kennedy, J. A.; Teissedre, P.-L.; Saucier, C. Ethylidene-bridged flavan-3-ols in red wine and correlation with wine age. *J. Agric. Food Chem.*, **2007** , 55, 6292 - 6299.

Acknowledgments

Collaborators:

J. DRINKINE, P. LOPES, J.A KENNEDY, PL TEISSEDE,
Y GLORIES

Fundings:

Yvon Mau SA, Amorim, CIVB, ANRT (Gov.)

The background of the slide is a grayscale micrograph showing a dense array of oval-shaped cells, likely from a plant stem. A semi-transparent grid is overlaid on the image. The text 'THANK YOU!' is centered in a bright yellow font.

THANK YOU !