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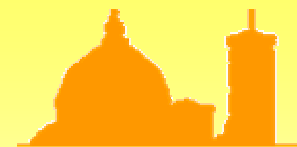
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29 August-3 September 2010 Florence (Italy)
30th European Congress on Molecular Spectroscopy



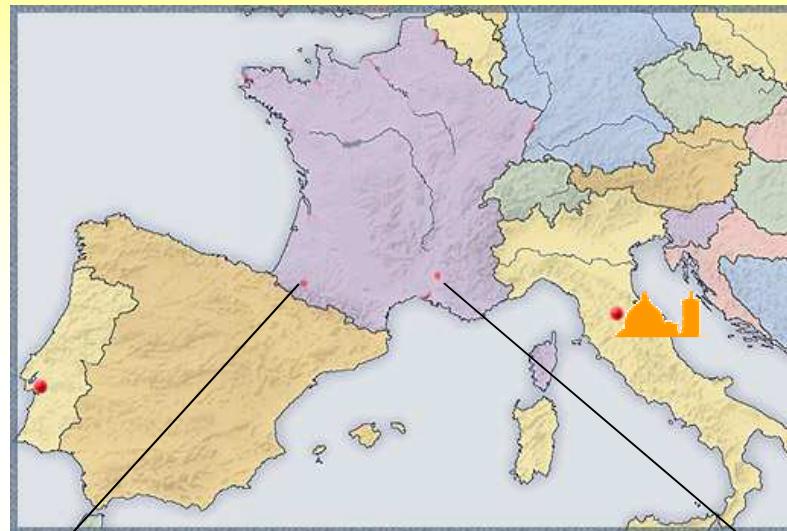
**Solid state complexation
of natural organic dyes with Al(III):
electronic and vibrational spectroscopies**

Sylvie Blanc

Tu Khai Nam Nguyen
Kevin Bourhis
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Carole Mathe

Catherine Vieillescazes



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Equipe Chimie Physique

Equipe Chimie Appliquée à l'Art et à l'Archéologie

Yellow of Avignon : short history

◆ Characteristics

- Yellow dyes extracted from fruits of *Rhamnus* species
- Tinctorial properties known since the Antiquity
- Employed in artistic paintings as yellow lakes
- Production in the area of Avignon (commercial place)



Livre des Jeux of Alphonse le Sage
1282 Escorial's Library

◆ History

- Lateran Council of 1215
discrimination of the Jews using yellow dye
(until the 18th century)

Preparation of Avignon yellow lakes (Stil-de-grain)

◆ Marcucci's « recipe »

- Powdering of dried immature *Rhamnus* berries
- Maceration under agitation during 24-48 hours
- Filtration to remove the residues
- Addition of alum ($KAl(SO_4)_2 \cdot 12 H_2O$)
- Precipitation of the mixture with an alcalinic carbonate



◆ Physico-chemical explanation provided

- Extraction of the dye during the maceration
- Complexation of the dye by the metallic ion Al^{3+} contained in alum
- Precipitation of the complex with an elevation of the pH from 5 to 12

⇒ formation of an inorganic matrix of amorphous aluminium hydroxide including the organic dyes

L. Marcucci, Saggio analytico-chimico sopra i colori minerali, 2nd ed., Rome (1816), 120-121

Objectives

◆ Extraction and characterization of the natural dyes

⇒ chromophore model

◆ Preparation of lakes without solvent

⇒ co-grinding dye and Al(III)
dilution in Al(OH)₃ matrix

◆ Characterisation of the materials by spectroscopy

UV-Visible and IR reflectance

⇒ color and Al coordination sites

Raman and fluorescence

⇒ Synthesis of a Avignon lake model

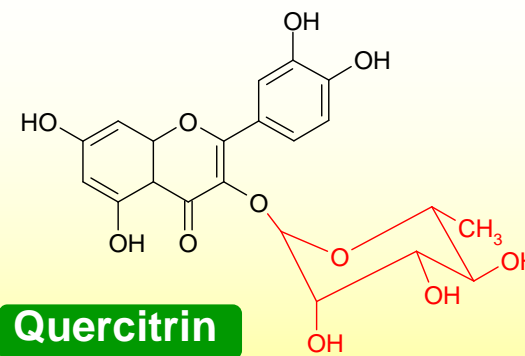
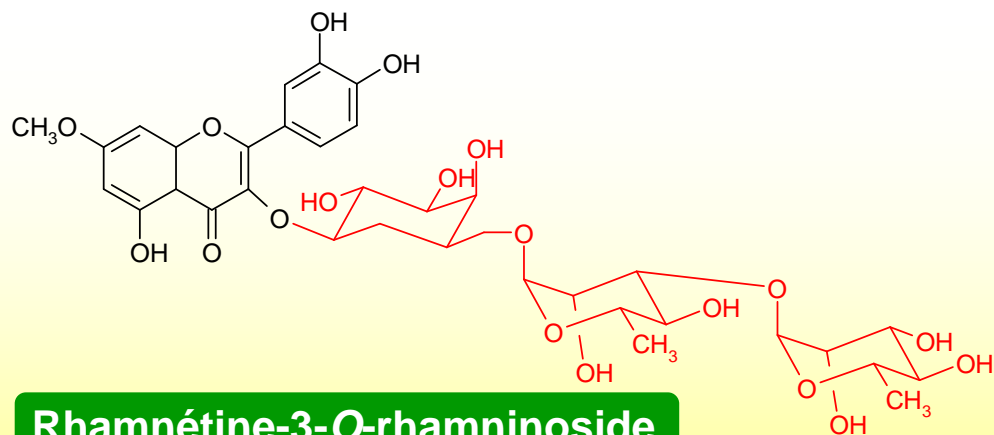
Yellow dyes of *Rhamnus catharticus*

◆ Optimization of the the extraction process

- quantity of *Rhamnus* berries
- solvent
- temperature
- time

H₂O
⇒ 1 h (maceration)
room T

◆ Separation and identification by HPLC-PDA

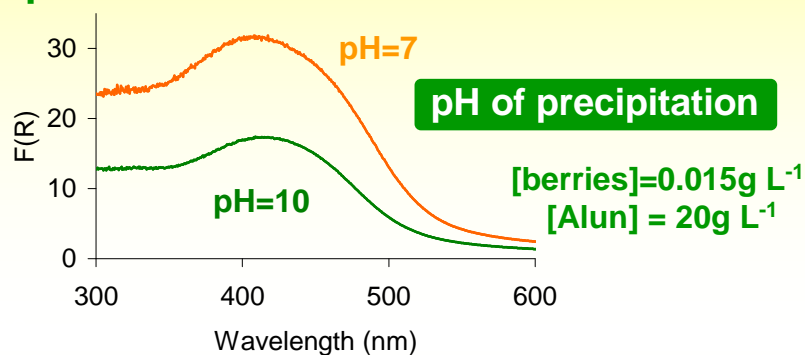


⇒ Two major extracted molecules : quercetin derivatives

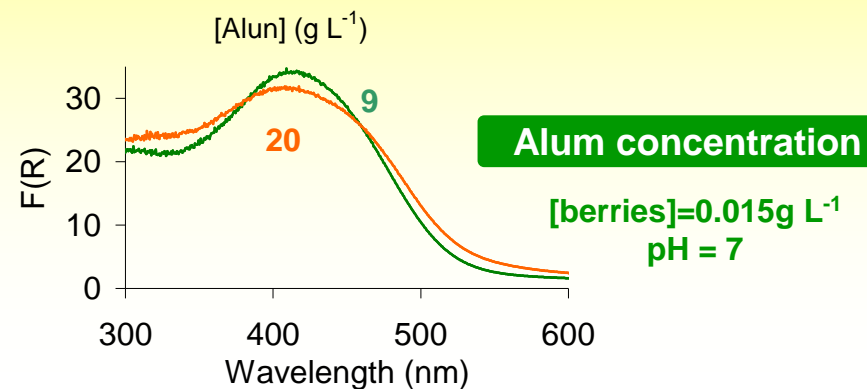
Natural and quercetine lake

◆ Natural lake

➤ Optimization of conditions



A precipitate obtained by mixing dye+alun+carbonate in solution

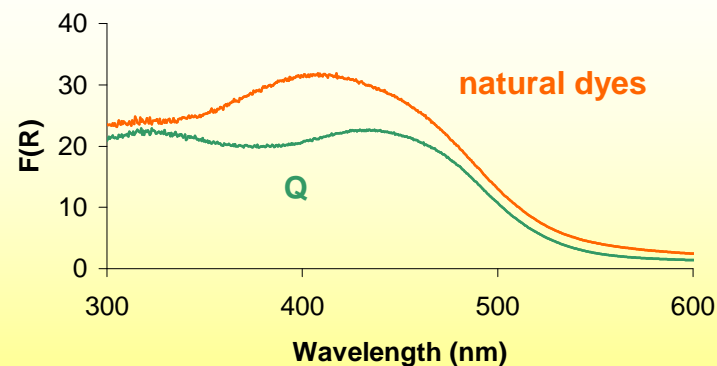


◆ Quercetine lake

➤ Parameters of preparation

$[\text{Q}] = 10^{-3} \text{ M}$; $[\text{Alun}] = 7 \text{ g L}^{-1}$
 Immediate precipitation at $\text{pH} = 7$ (Na_2CO_3)

⇒ $[\text{berries}] = 0.015 \text{ g L}^{-1}$; $[\text{Alun}] = 9 \text{ g L}^{-1}$; $\text{pH} = 7$

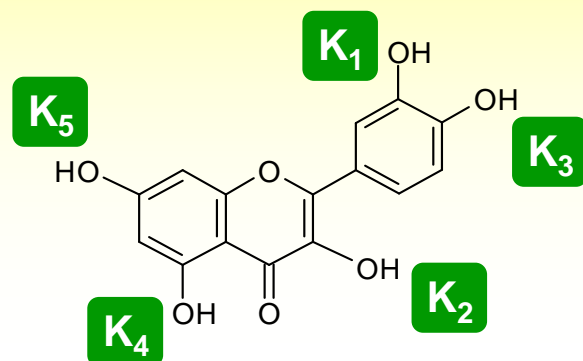


⇒ Quercetin : chromophore model

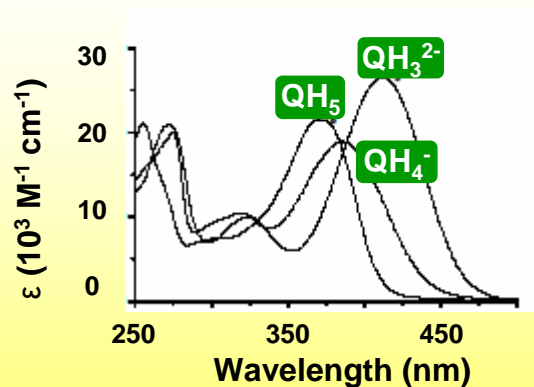
Quercetin in solution

◆ Acid-base properties

➤ Several protonation sites

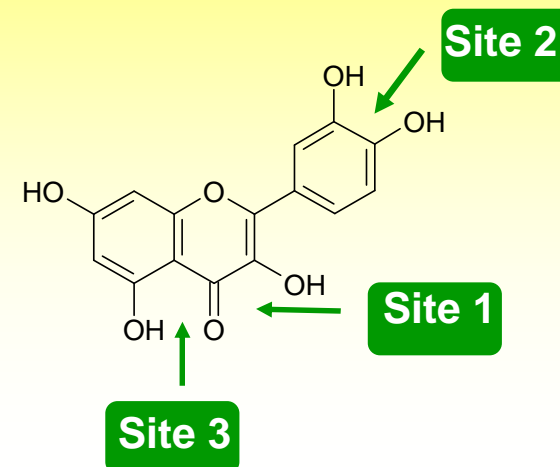


➤ Absorption spectrum versus pH



◆ Al(III) complexation

➤ Several coordination sites sites



➤ Several complexes

1 cation : AlQ , AlQ_2 , AlQ_3 ,
2 cations : Al_2Q , Al_2Q_3

Solid state properties?

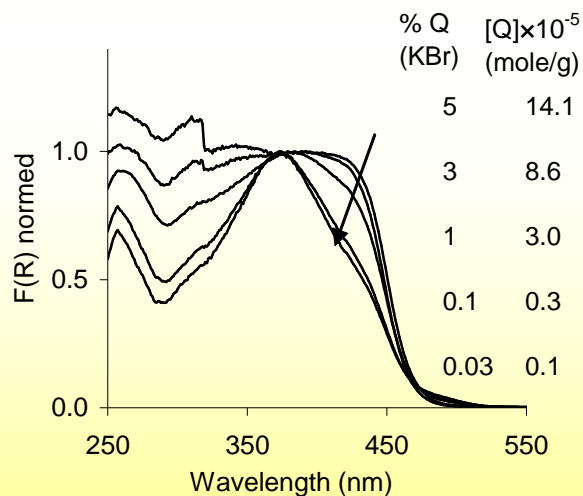
L. Dangleterre, J.P. Cornard, C. Lapouge, Polyhedron 27 (2008) 1581; T.L. Lin, B.Z. Yan, G.F. Hu, M. Wang, Chinese Chemical Letters 17 (2006) 937; R.F.V. De Souza, W.F. de Giovanni, Spectrochim. Acta, Part A 61 (2005) 1985; X. Chang, S. Wang, H. Luo, G. Gong, J. Fluoresc. 13 (2003) 421; J.P. Cornard, J.C. Merlin, J. Inorg. Biochem. 92 (2002) 19; A.C. Gutierrez, M.H. Gehlen, Spectrochim. Acta, Part A 58 (2002) 83; E.A. Saad, L.H. Khalil, M.T.M. Zaki, A.A.A. El-Ella, Microchim. Acta 140 (2002) 87; H. Deng, G.J. Van Berkel, J. Mass Spectrom. 33 (1998) 1080

Quercetin powder

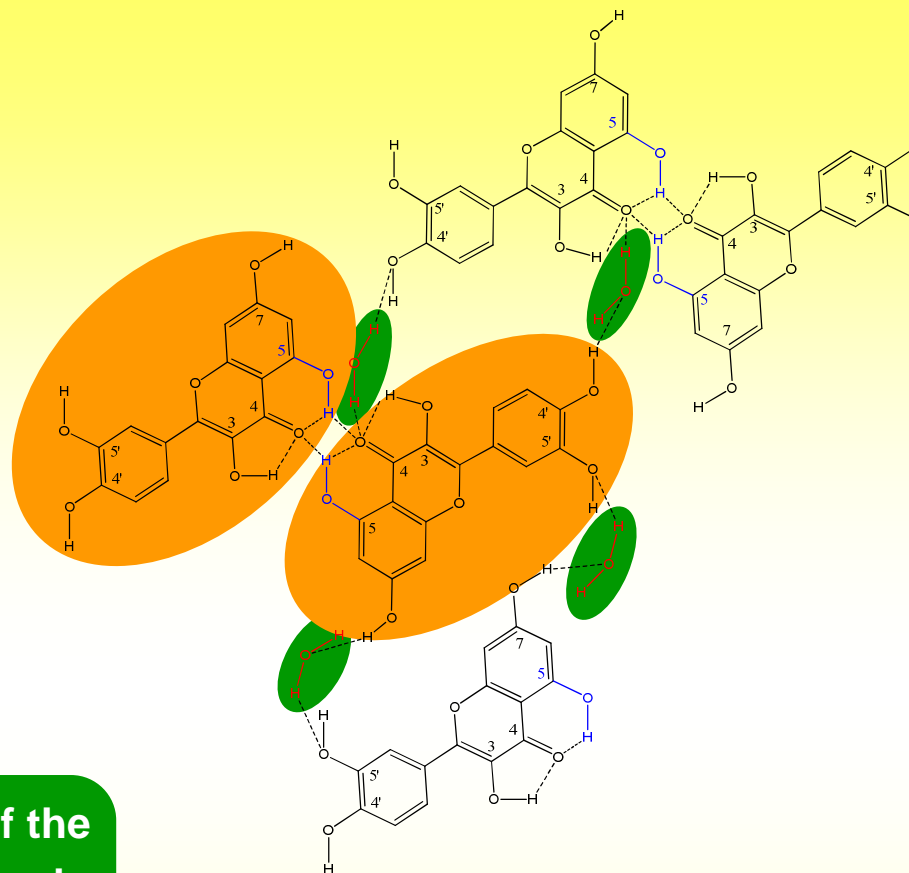
◆ Structure

- Dimer
- Dihydrate

◆ DRUV



broadening of the absorption band with increasing concentration



Monomer ↔ dimer?

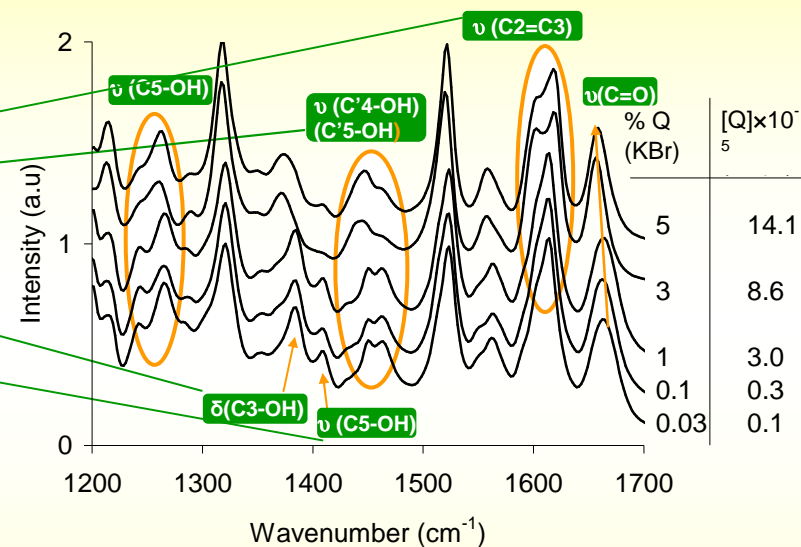
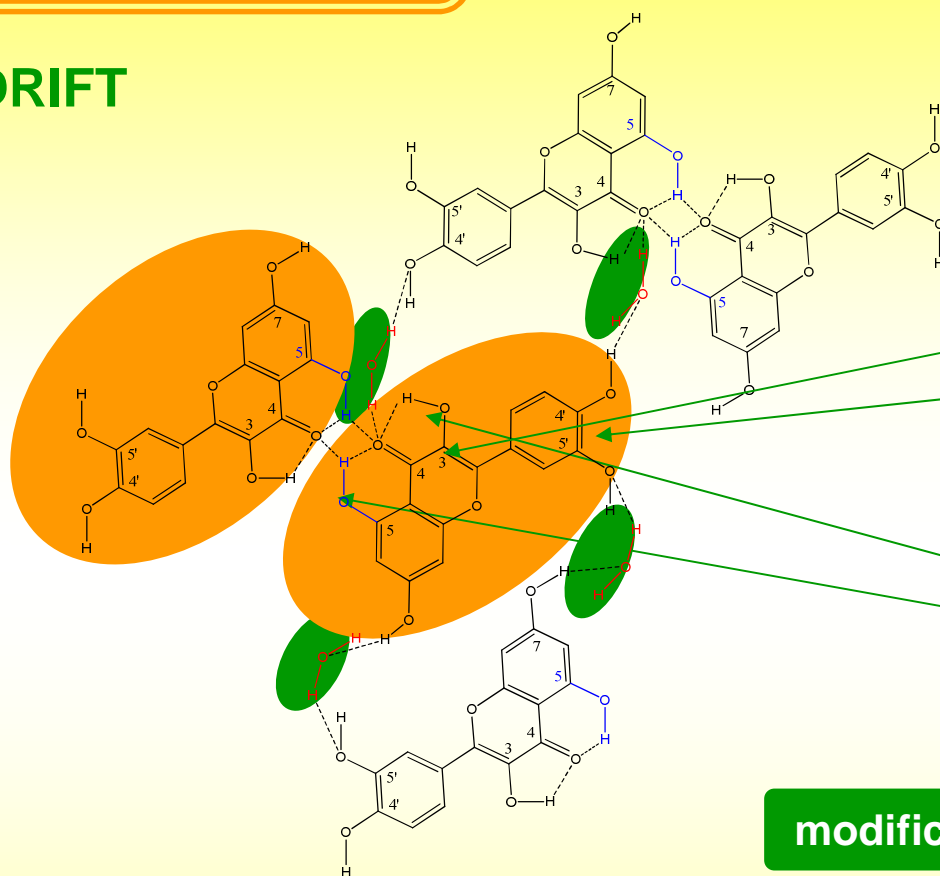
Rearrangement of water molecules?

G.Z. Jin, Y. Yamagata, K. Tomita, Acta Cryst. C46 (1990) 310; M. Rossi, L.F. Rickles, W.A. Halpin. Bioorg. Chem.14 (1986) 55
J.P. Cornard, J.C.Merlin, A.C. Boudet, L. Vrielynck, Biospectroscopy (1997) 3 183

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Quercetin powder

◆ DRIFT



modifications around the carbonyl group with [Q]

Rupture of intermolecular hydrogen bond
Dimer \Rightarrow Monomer

G.Z. Jin, Y. Yamagata, K. Tomita, Acta Cryst. C46 (1990) 310; M. Rossi, L.F. Rickles, W.A. Halpin. Bioorg. Chem.14 (1986) 55
J.P. Cornard, J.C.Merlin, A.C. Boudet, L. Vrielynck, Biospectroscopy (1997) 3 183

Solid state complexation of natural organic dyes with Al(III):electronic and vibrational spectroscopies

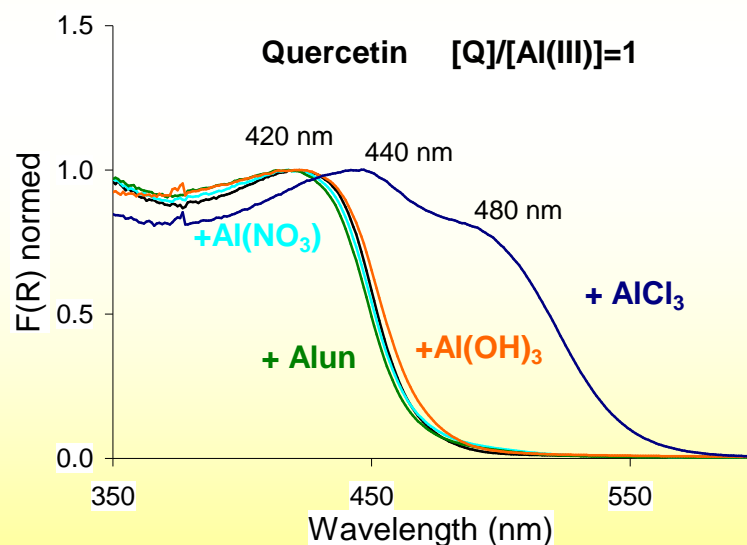
Solid state complexation of quercetin with Al(III)

◆ Cation

quercetin + alun + $\text{Al}(\text{NO}_3)_3$ + AlCl_3



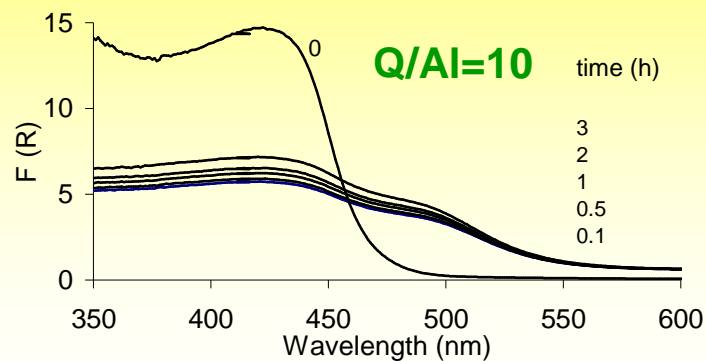
◆ DRUV



⇒ Complexation
only with AlCl_3

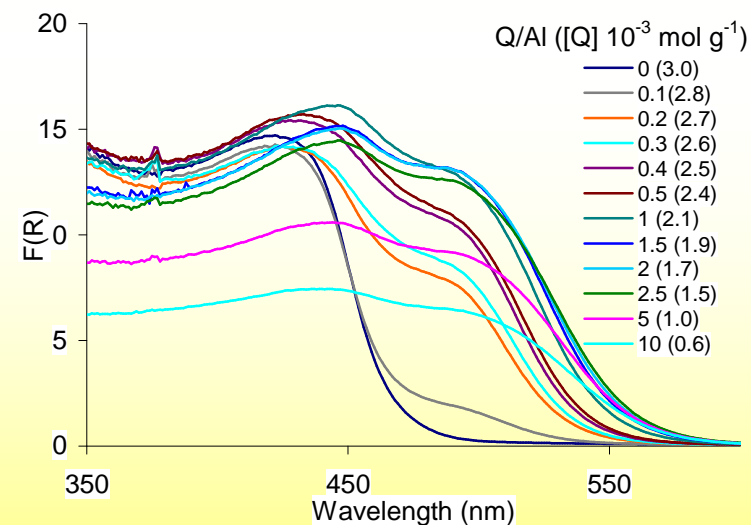
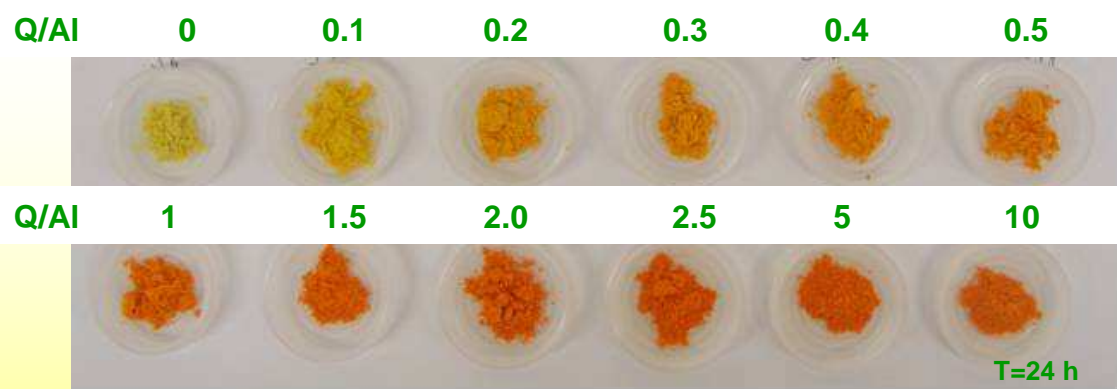
Solid state AlCl_3 complex : DRUV

◆ Kinetics



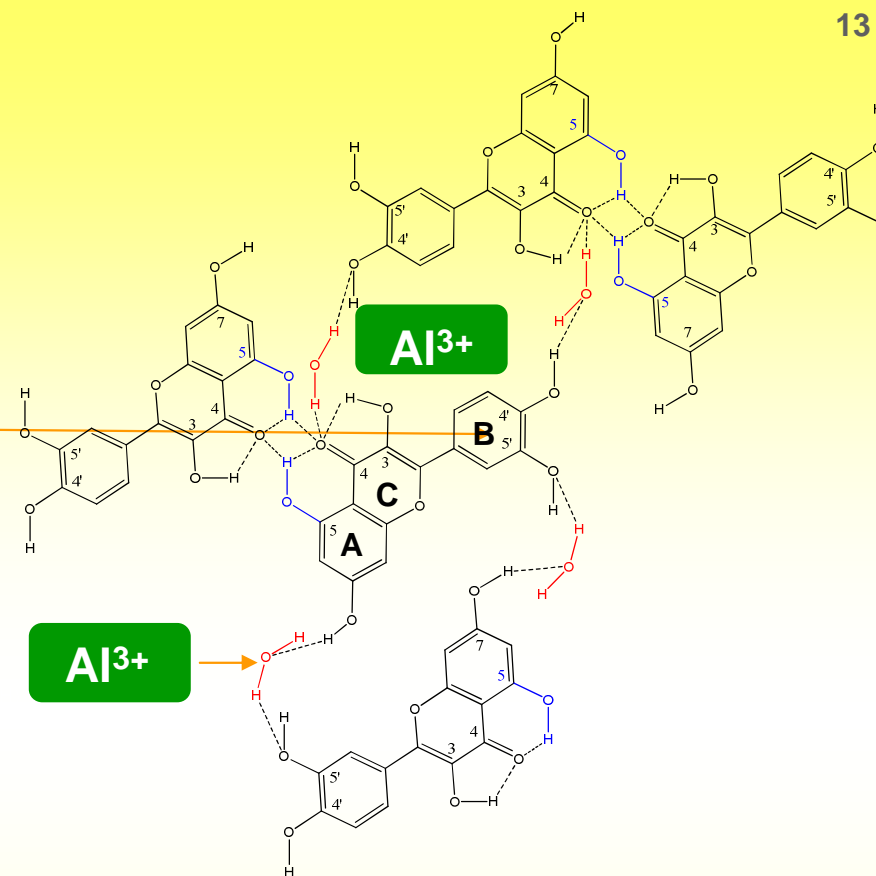
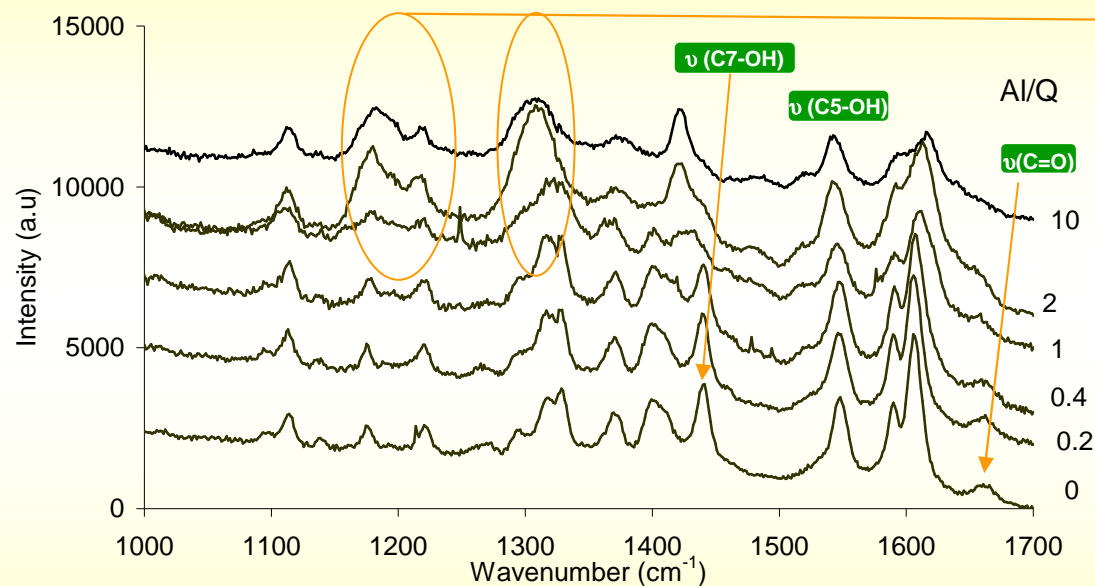
complete reaction
in few hours

◆ Al(III) concentration



⇒ two absorption bands around 450 and 490 nm

Solid state AlCl_3 complex : Raman

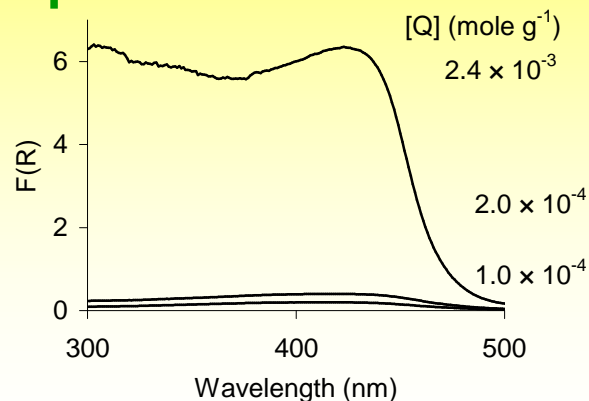


$\text{Al}^{3+} \rightleftharpoons$ water molecules
phenol coordination

J.P. Cornard, J.C. Merlin, A.C. Boudet, L. Vrielynck, Biospect, 3 (1997) 183; T. Teslova¹, C. Corredor, R. Livingstone, T. Spataru, R.L. Birke, J.R. Lombardi, M. V. Cañamares, M. Leona, JRS 38 (2007) 802

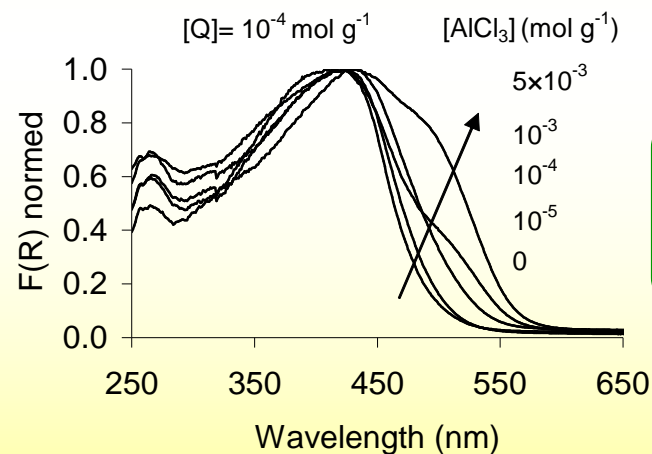
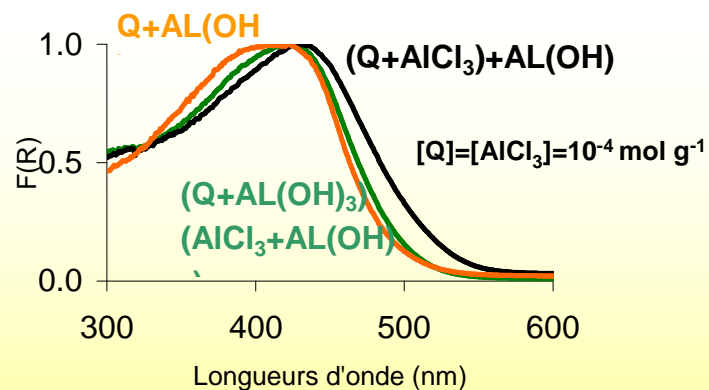
Solid state AlCl_3 complex in $\text{Al}(\text{OH})_3$ Matrix

➤ Dilution of quercetin



Dimer characteristics
 ⇒ Quantitative analysis

➤ Al(III) complex



Modification of the complex reflectance with $\text{Al}(\text{OH})_3$

No complexation but interaction between complex and $\text{Al}(\text{OH})_3$

Solid state AlCl_3 complex and quercetin lake

◆ Classical quercetin Lake :

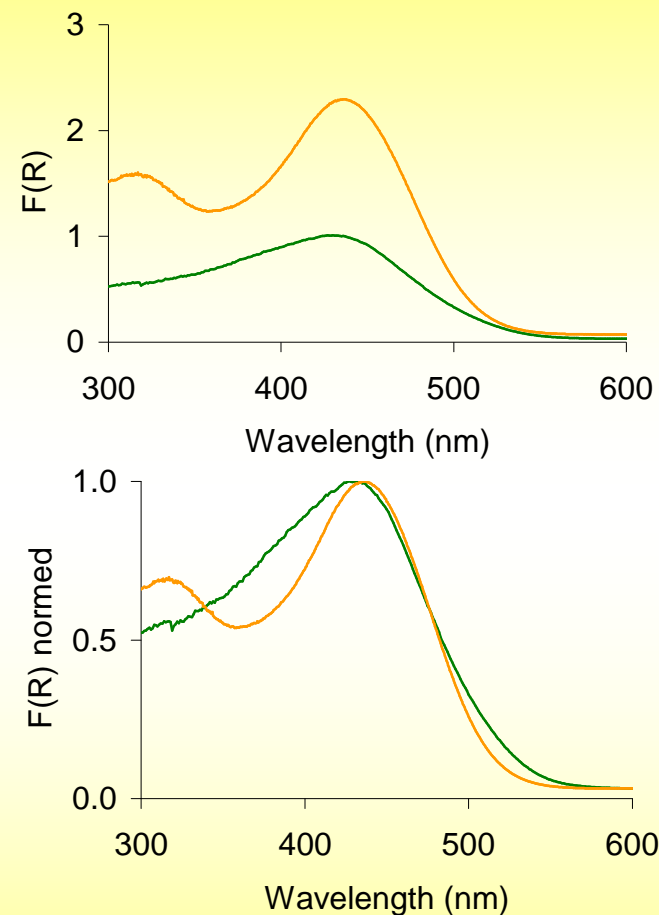
precipitate obtained by mixing
quercetin +alun+carbonate in solution

$[\text{Q}] = 10^{-3} \text{ M}$; $[\text{Alun}] = 30 \text{ g L}^{-1}$
Immediate precipitapn at $\text{pH} = 7$ (Na_2CO_3)

◆ Solid state quercetin lake :

$(\text{Q} + \text{AlCl}_3) + \text{Al}(\text{OH})_3$

$[\text{Q}] = [\text{AlCl}_3] = 10^{-4} \text{ M}$

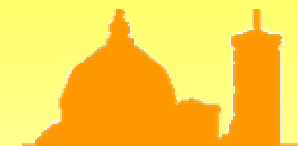


Similar UV-Visible reflectance spectrum

Conclusion

- ◆ Identification of the yellow dyes of *Rhamnus catharticus*
 - Quercetin as chromophore model for Avignon Lake
- ◆ Quercetin powder
 - monomer and dimer observed by DRIFT and DRUV
- ◆ Solid state complexation of quercetin with $AlCl_3$
 - observed by DRUV
 - reaction with water molecules showed by Raman
- ◆ Complex dilution in $Al(OH)_3$
 - interaction between the complex and the matrix
- ◆ Solid state quercetin lake
 - similar reflectance spectrum as classical quercetin lake

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Thank you for your attention

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